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- [54] METHOD FOR MAKING INTERNAL SHAPES IN A METAL MATRIX COMPOSITE BODY
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- [21] Appl. No.: 73,996
- [22] Filed: Jun. 9, 1993

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

00714492/1983European Pat. Off.009435311/1983European Pat. Off.01157428/1984European Pat. Off.03239457/1989European Pat. Off.034095711/1989European Pat. Off.03649634/1990European Pat. Off.

Related U.S. Application Data

 [63] Continuation of Ser. No. 804,467, Dec. 5, 1991, abandoned, which is a continuation of Ser. No. 521,506, May 10, 1990, abandoned.

[56] **References Cited** U.S. PATENT DOCUMENTS

3,031,340	4/1962	Circadot 117/110
	•	Girardot 117/118
3,149,409		Maruhn
3,364,976	-	Reding et al 164/63
3,396,777	8/1968	Reding, Jr 164/97
3,450,189	6/1969	MacDonald 164/97
3,547,180	12/1970	Cochran et al 164/61
3,608,170	9/1971	Larson et al
3,718,441	2/1973	Landingham
3,864,154	2/1975	Gazza et al 29/123 B
3,868,267	2/1975	Gazza et al 117/22
3,915,699	10/1975	Umehara et al 75/208 R
3,969,553	7/1976	Kondo et al 427/299
3,970,136	7/1976	Cannell et al 164/108
4,082,864	4/1978	Kendall et al 427/248
4,232,091	11/1980	Grimshaw et al 428/472
4,376,803	3/1983	Katzman 428/408
4,376,804	3/1983	Katzman 428/408
4,450,207	5/1984	Donomoto et al 428/614
4,473,103	9/1984	Kenney et al 164/97
4,559,246	12/1985	Jones
4,570,316	2/1986	Sakamaki et al 29/156.8 R
4,630,665	12/1986	Novak et al
4,657,065		Wada et al 164/461
-,,		

0307703 + 71990	European Fai. On.
2819076 10/1979	Germany .
0144441 8/1983	Japan.
2156718 10/1985	United Kingdom 164/102
2173134 10/1986	United Kingdom 164/97
8103633 12/1981	WIPO .

OTHER PUBLICATIONS

International Search Report for International Patent Application Ser. No. PCT/US91/03196 (see attached Search Report).

(List continued on next page.)

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[57] ABSTRACT

The present invention relates to a novel process for forming internal shapes in metal matrix composite bodies. Particularly, an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere are in communication with a filler material or a preform, at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler material or preform. Additionally, the filler material or preform may contain a mandrel which is capable of surviving the infiltration process, said mandrel being removed after infiltration has occurred. Such spontaneous infiltration occurs without the requirement for the application of any pressure or vacuum.

22 Claims, 2 Drawing Sheets



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U.S. PATENT DOCUMENTS

4,712,600		Hamajima 164/97
4,713,111		Cameron et al 75/68 R
4,753,690		Wada et al 148/11.5 A
4,777,097	10/1988	Kubo et al 428/614
4,802,524		Donomoto 164/97
4,820,461	4/1989	Creber
4,828,008	5/1989	White et al 164/66.1
4,871,008	10/1989	Dwivedi et al 164/6
4,891,875	1/1990	Soichi
4,932,099	6/1990	Corwin 164/97
4,935,055	6/1990	Aghajanian 164/66.1
4,972,898	11/1990	Cole
5,000,245	3/1991	White et al 164/97
5,004,036	4/1991	Becker
5,005,631	4/1991	Dwivedi 164/67.1

Journal of Materials Science, vol. 22, No. 1, pp. 1-16, Jan. 1987.

G. R. Edwards and D. L. Olson, "The Infiltration Kinetics of Aluminum in Silicon Carbide Compacts", Annual Report from Center for Welding Research, Colorado School of Mines, under ONR Contract No. M00014-85-K-0451, DTIC Report AD-A184 682, Jul. 1987.

A. Mortensen, M. N. Gungor, J. A. Cornie, and M. C. Flemings "Alloy Microstructures in Cast Metal Matrix Composites", Journal of Metals, vol. 38, No. 3, pp. 30-35, Mar. 1986.

OTHER PUBLICATIONS

F. Delannay, L. Froyen, and A. Deruyttere, "Review: The Wetting of Solids by Molten Metals and Its Relation to the Preparation of Metal-Matrix Composites", A. Mortensen, J. A. Cornie, and M. C. Flemings, "Solidification Processing of Metal-Matrix Composites", Journal of Metals, vol. 40, No. 2, pp. 12–19, Feb. 1988.
B. D. Sparks and F. W. Meadus, "The Development of an Infiltrated Lead/Iron Composite Material For Use as a Non-toxic Bird Shot", Composites, pp. 37–39, Jan. 1978.

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METHOD FOR MAKING INTERNAL SHAPES IN A METAL MATRIX COMPOSITE BODY

This is a continuation of copending application Ser. 5 No. 07/804,467 filed on Dec. 5. 1991, and now abandoned.

FIELD OF INVENTION

The present invention relates to a novel process for 10 forming internal shapes in metal matrix composite bodies. Particularly, an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere are in communication with a filler material or a preform, at least at some point during the process, 15 which permits molten matrix metal to spontaneously infiltrate the filler material or preform. Additionally, the filler material or preform may contain a shape defining means which is capable of surviving the infiltration process, said shape defining means being removed after 20 infiltration has occurred. Such spontaneous infiltration occurs without the requirement for the application of any pressure or vacuum.

characteristics of the products attainable. The volume fraction of the ceramic phase in the composite is limited typically, in the case of particulates, to about 40 percent. Also, the pressing operation poses a limit on the practical size attainable. Only relatively simple product shapes are possible without subsequent processing (e.g., forming or machining) or without resorting to complex presses. Also, nonuniform shrinkage during sintering can occur, as well as nonuniformity of microstructure due to segregation in the compacts and grain growth.

U.S. Pat. No. 3,970,136, granted Jul. 20, 1976, to J. C. Cannell et al., describes a process for forming a metal matrix composite incorporating a fibrous reinforcement, e.g. silicon carbide or alumina whiskers, having a predetermined pattern of fiber orientation. The composite is made by placing parallel mats or felts of coplanar fibers in a mold with a reservoir of molten matrix metal, e.g., aluminum, between at least some of the mats, and applying pressure to force molten metal to penetrate the mats and surround the oriented fibers. Molten metal may be poured onto the stack of mats while being forced under pressure to flow between the mats. Loadings of up to about 50% by volume of reinforcing fibers in the composite have been reported. The above-described infiltration process, in view of its dependence on outside pressure to force the molten matrix metal through the stack of fibrous mats, is subject to the vagaries of pressure-induced flow processes, i.e., possible non-uniformity of matrix formation, porosity, etc. Non-uniformity of properties is possible even though molten metal may be introduced at a multiplicity of sites within the fibrous array. Consequently, complicated mat/reservoir arrays and flow pathways need to be provided to achieve adequate and uniform penetration of the stack of fiber mats. Also, the aforesaid pressure-infiltration method allows for only a relatively low reinforcement to matrix volume fraction to be achieved because of the difficulty inherent in infiltrating a large mat volume. Still further, molds are required to contain the molten metal under pressure, which adds to the expense of the process. Finally, the aforesaid process, limited to infiltrating aligned particles or fibers, is not directed to formation of aluminum metal matrix composites reinforced with materials in the form of randomly oriented particles, whiskers or fibers. In the fabrication of aluminum matrix-alumina filled composites, aluminum does not readily wet alumina, thereby making it difficult to form a coherent product. 50 Various solutions to this problem have been suggested. One such approach is to coat the alumina with a metal (e.g., nickel or tungsten), which is then hot-pressed along with the aluminum. In another technique, the aluminum is alloyed with lithium, and the alumina may be coated with silica. However, these composites exhibit variations in properties, or the coatings can degrade the filler, or the matrix contains lithium which can affect the matrix properties. U.S. Pat. No. 4,232,091 to R. W. Grimshaw et al., overcomes certain difficulties in the art which are encountered in the production of aluminum matrixalumina composites. This patent describes applying pressures of 75-375 kg/cm² to force molten aluminum (or molten aluminum alloy) into a fibrous or whisker 65 mat of alumina which has been preheated to 700° to 1050° C. The maximum volume ratio of alumina to metal in the resulting solid casting was 0.25/1. Because of its dependency on outside force to accomplish infil-

BACKGROUND OF THE INVENTION

Composite products comprising a metal matrix and a strengthening or reinforcing phase such as ceramic particulates, whiskers, fibers or the like, show great promise for a variety of applications because they combine some of the stiffness and wear resistance of the 30 reinforcing phase with the ductility and toughness of the metal matrix. Generally, a metal matrix composite will show an improvement in such properties as strength, stiffness, contact wear resistance, coefficient of thermal expansion (C.T.E.), density, thermal conduc- 35 tivity and elevated temperature strength retention relative to the matrix metal in monolithic form, but the degree to which any given property may be improved depends largely on the specific constituents, their volume or weight fraction, and how they are processed in 40 forming the composite. In some instances, the composite also may be lighter in weight than the matrix metal per se. Aluminum matrix composites reinforced with ceramics such as silicon carbide in particulate, platelet, or whisker form, for example, are of interest because of 45 their higher specific stiffness (e.g., elastic modulus over density), wear resistance, thermal conductivity, low coefficient of thermal expansion (C.T.E.) and high temperature strength and/or specific strength (e.g., strength over density) relative to aluminum. Various metallurgical processes have been described for the fabrication of aluminum matrix composites, including methods based on powder metallurgy techniques and liquid-metal infiltration techniques which make use of pressure casting, vacuum casting, stirring, 55 and wetting agents. With powder metallurgy techniques, the metal in the form of a powder and the reinforcing material in the form of a powder, whiskers, chopped fibers, etc., are admixed and then either coldpressed and sintered, or hot-pressed. The maximum 60 ceramic volume fraction in silicon carbide reinforced aluminum matrix composites produced by this method has been reported to be about 25 volume percent in the case of whiskers, and about 40 volume percent in the case of particulates.

The production of metal matrix composites by powder metallurgy techniques utilizing conventional processes imposes certain limitations with respect to the

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tration, this process is subject to many of the same deficiencies as that of Cannell et al.

European Patent Application Publication No. 115,742 describes making aluminum-alumina composites, especially useful as electrolytic cell components, by 5 filling the voids of a preformed alumina matrix with molten aluminum. The application emphasizes the nonwettability of alumina by aluminum, and therefore various techniques are employed to wet the alumina throughout the preform. For example, the alumina is 10 coated with a wetting agent of a diboride of titanium, zirconium, hafnium, or niobium, or with a metal, i.e., lithium, magnesium, calcium, titanium, chromium, iron, cobalt, nickel, zirconium, or hafnium. Inert atmoting. This reference also shows applying pressure to cause molten aluminum to penetrate an uncoated matrix. In this aspect, infiltration is accomplished by evacuating the pores and then applying pressure to the molten aluminum in an inert atmosphere, e.g., argon. Alter- 20 natively, the preform can be infiltrated by vapor-phase aluminum deposition to wet the surface prior to filling the voids by infiltration with molten aluminum. To assure retention of the aluminum in the pores of the preform, heat treatment, e.g., at 1400° to 1800° C., in 25 either a vacuum or in argon is required. Otherwise, either exposure of the pressure infiltrated material to gas or removal of the infiltration pressure will cause loss of aluminum from the body. The use of wetting agents to effect infiltration of an 30 alumina component in an electrolytic cell with molten metal is also shown in European Patent Application Publication No. 94353. This publication describes production of aluminum by electrowinning with a cell having a cathodic current feeder as a cell liner or sub- 35 strate. In order to protect this substrate from molten cryolite, a thin coating of a mixture of a wetting agent and solubility suppressor is applied to the alumina substrate prior to start-up of the cell or while immersed in the molten aluminum produced by the electrolytic pro- 40 cess. Wetting agents disclosed are titanium, zirconium, hafnium, silicon, magnesium, vanadium, chromium, niobium, or calcium, and titanium is stated as the preferred agent. Compounds of boron, carbon and nitrogen are described as being useful in suppressing the solubil- 45 ity of the wetting agents in molten aluminum. The reference, however, does not suggest the production of metal matrix composites, nor does it suggest the formation of such a composite in, for example, a nitrogen atmosphere. In addition to application of pressure and wetting agents, it has been disclosed that an applied vacuum will aid the penetration of molten aluminum into a porous ceramic compact. For example, U.S. Pat. No. 3,718,441, granted Feb. 27, 1973, to R. L. Landingham, reports 55 infiltration of a ceramic compact (e.g., boron carbide, alumina and beryllia) with either molten aluminum, beryllium, magnesium, titanium, vanadium, nickel or chromium under a vacuum of less than 10^{-6} torr. A vacuum of 10^{-2} to 10^{-6} torr resulted in poor wetting of 60 the ceramic by the molten metal to the extent that the metal did not flow freely into the ceramic void spaces. However, wetting was said to have improved when the vacuum was reduced to less than 10^{-6} torr. Gazza et al., also shows the use of vacuum to achieve infiltration. This patent describes loading a cold-pressed compact of AlB_{12} powder onto a bed of cold-pressed

aluminum powder. Additional aluminum was then positioned on top of the AlB_{12} powder compact. The crucible, loaded with the AlB₁₂ compact "sandwiched" between the layers of aluminum powder, was placed in a vacuum furnace. The furnace was evacuated to approximately 10^{-5} torr to permit outgassing. The temperature was subsequently raised to 1100° C. and maintained for a period of 3 hours. At these conditions, the molten aluminum penetrated the porous AlB₁₂ compact.

U.S. Pat. No. 3,364,976, granted Jan. 23, 1968 to John N. Reding et al., discloses the concept of creating a self-generated vacuum in a body to enhance penetration of a molten metal into the body. Specifically, it is disclosed that a body, e.g., a graphite mold, a steel mold, or spheres, such as argon, are employed to facilitate wet- 15 a porous refractory material, is entirely submerged in a molten metal. In the case of a mold, the mold cavity, which is filled with a gas reactive with the metal, communicates with the externally located molten metal through at least one orifice in the mold. When the mold is immersed into the melt, filling of the cavity occurs as the self-generated vacuum is produced from the reaction between the gas in the cavity and the molten metal. Particularly, the vacuum is a result of the formation of a solid oxidized form of the metal. Thus, Reding et al. disclose that it is essential to induce a reaction between gas in the cavity and the molten metal. However, utilizing a mold to create a vacuum may be undesirable because of the inherent limitations associated with use of a mold. Molds must first be machined into a particular shape; then finished, machined to produce an acceptable casting surface on the mold; then assembled prior to their use; then disassembled after their use to remove the cast piece therefrom; and thereafter reclaim the mold, which most likely would include refinishing surfaces of the mold or discarding the mold if it is no longer acceptable for use. Machining of a mold into a complex shape can be very costly and time-consuming. Moreover, removal of a formed piece from a complexshaped mold can also be difficult (i.e., cast pieces having a complex shape could be broken when removed from the mold). Still further, while there is a suggestion that a porous refractory material can be immersed directly in a molten metal without the need for a mold, the refractory material would have to be an integral piece because there is no provision for infiltrating a loose or separated porous material absent the use of a container mold (i.e., it is generally believed that the particulate material would typically disassociate or float apart when placed in a molten metal). Still further, if it was 50 desired to infiltrate a particulate material or loosely formed preform, precautions should be taken so that the infiltrating metal does not displace at least portions of the particulate or preform resulting in a non-homogeneous microstructure. Accordingly, there has been a long felt need for a simple and reliable process to produce internally and externally shaped metal matrix composites which does not rely upon the use of applied pressure or vacuum (whether externally applied or internally created), or damaging wetting agents to create a metal matrix embedding another material such as a ceramic material. Moreover, there has been a long felt need to minimize the amount of final machining operations needed to produce a metal matrix composite bodies having shaped U.S. Pat. No. 3,864,154, granted Feb. 4, 1975, to G. E. 65 interior and exterior portions. The present invention satisfies these needs by providing a spontaneous infiltration mechanism for infiltrating a material (e.g., a ceramic material), which can be formed into a preform

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having predetermined interior and exterior shapes, with molten matrix metal (e.g., aluminum) in the presence of an infiltrating atmosphere (e.g., nitrogen) under normal atmospheric pressures so long as an infiltration enhancer precursor and/or infiltration enhancer is present 5 at least at some point during the process.

DESCRIPTION OF COMMONLY OWNED U.S. PATENTS AND PATENT APPLICATIONS

The subject matter of this application is related to 10 that of several co-owned Patents and several other copending and co-owned patent applications. Particularly, the patent and other copending patent applications and issued Patents describe novel methods for making metal matrix composite materials (hereinafter 15 sometimes referred to as "Commonly Owned Metal Matrix Patents and Patent Applications"). A novel method of making a metal matrix composite material is disclosed in Commonly Owned U.S. Pat. No. 4,828,008, which issued May 9, 1989, from U.S. patent 20 application Ser. No. 07/049,171, filed May 13, 1987, in the names of White et al., and entitled "Metal Matrix Composites", now U.S. Pat. No. 4,828,008, which issued on May 9, 1989, and which published in the EPO on Nov. 17, 1988, as Publication No. 0291441. Accord- 25 ing to the method of this White et al. invention, a metal matrix composite is produced by infiltrating a permeable mass of filler material (e.g., a ceramic or a ceramiccoated material) with molten aluminum containing at least about 1 percent by weight magnesium, and prefer- 30 ably at least about 3 percent by weight magnesium. Infiltration occurs spontaneously without the application of external pressure or vacuum. A supply of the molten metal alloy is contacted with the mass of filler material at a temperature of at least about 675° C. in the 35 presence of a gas comprising from about 10 to 100 percent, and preferably at least about 50 percent, nitrogen by volume, and a remainder of the gas, if any, being a nonoxidizing gas, e.g., argon. Under these conditions, the molten aluminum alloy infiltrates the ceramic mass 40 under normal atmospheric pressures to form an aluminum (or aluminum alloy) matrix composite. When the desired amount of filler material has been infiltrated with the molten aluminum alloy, the temperature is lowered to solidify the alloy, thereby forming a solid 45 metal matrix structure that embeds the reinforcing filler material. Usually, and preferably, the supply of molten alloy delivered will be sufficient to permit the infiltration to proceed essentially to the boundaries of the mass of filler material. The amount of filler material in the 50 aluminum matrix composites produced according to the White et al. invention may be exceedingly high. In this respect, filler to alloy volumetric ratios of greater than 1:1 may be achieved. Under the process conditions in the aforesaid White 55 et al. invention, aluminum nitride can form as a discontinuous phase dispersed throughout the aluminum matrix. The amount of nitride in the aluminum matrix may vary depending on such factors as temperature, alloy composition, gas composition and filler material. Thus, 60 by controlling one or more such factors in the system, it is possible to tailor certain properties of the composite. For some end use applications, however, it may be desirable that the composite contain little or substantially no aluminum nitride. 65

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choice of a balance between infiltration kinetics and nitride formation.

An example of suitable barrier means for use with metal matrix composite formation is described in Commonly Owned U.S. patent application Ser. No. 07/141,642, filed Jan. 7, 1988, in the names of Michael K. Aghajanian et al., and entitled Method of Making Metal Matrix Composite with the Use of a Barrier, now U.S. Pat. No. 4,935,055, which issued on Jun. 19, 1990, and which published in the EPO on Jul. 12, 1989, as Publication No. 0323945. According to the method of this Aghajanian et al. invention, a barrier means (e.g., particulate titanium diboride or a graphite material such as a flexible graphite foil product sold by Union Carbide under the trade name GRAFOIL (R) is disposed on a defined surface boundary of a filler material and matrix alloy infiltrates up to the boundary defined by the barrier means. The barrier means is used to inhibit, prevent, or terminate infiltration of the molten alloy, thereby providing net, or near net, shapes in the resultant metal matrix composite. Accordingly, the formed metal matrix composite bodies have an outer shape which substantially corresponds to the inner shape of the barrier means. The method of U.S. Pat. No. 4,828,008 was improved upon by Commonly Owned and Copending U.S. patent application Ser. No. 07/517,541, filed Apr. 24, 1990, which is continuation of U.S. patent application Ser. No. 07/168,284, filed Mar. 15, 1988, in the names of Michael K. Aghajanian and Marc S. Newkirk and entitled Metal Matrix Composites and Techniques for Making the Same, and which published in the EPO on Sep. 20, 1989, as Publication No. 0333629. In accordance with the methods disclosed in this U.S. patent application, a matrix metal alloy is present as a first source of metal and as a reservoir of matrix metal alloy which communicates with the first source of molten metal due to, for example, gravity flow. Particularly, under the conditions described in this patent application, the first source of molten matrix alloy begins to infiltrate the mass of filler material under normal atmospheric pressures and thus begins the formation of a metal matrix composite. The first source of molten matrix metal alloy is consumed during its infiltration into the mass of filler material and, if desired, can be replenished, preferably by a continuous means, from the reservoir of molten matrix metal as the spontaneous infiltration continues. When a desired amount of permeable filler has been spontaneously infiltrated by the molten matrix alloy, the temperature is lowered to solidify the alloy, thereby forming a solid metal matrix structure that embeds the reinforcing filler material. It should be understood that the use of a reservoir of metal is simply one embodiment of the invention described in this patent application and it is not necessary to combine the reservoir embodiment with each of the alternate embodiments of the invention disclosed therein, some of which could also be benefi-

cial to use in combination with the present invention.

It has been observed that higher temperatures favor infiltration but render the process more conducive to nitride formation. The White et al. invention allows the The reservoir of metal can be present in an amount such that it provides for a sufficient amount of metal to infiltrate the permeable mass of filler material to a predetermined extent. Alternatively, an optional barrier means can contact the permeable mass of filler on at least one side thereof to define a surface boundary.

Moreover, while the supply of molten matrix alloy delivered should be at least sufficient to permit spontaneous infiltration to proceed essentially to the boundaries (e.g., barriers) of the permeable mass of filler mate-

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rial, the amount of alloy present in the reservoir could exceed such sufficient amount so that not only will there be a sufficient amount of alloy for complete infiltration, but excess molten metal alloy could remain and be attached to the metal matrix composite body. Thus, 5 when excess molten alloy is present, the resulting body will be a complex composite body (e.g., a macrocomposite), wherein an infiltrated ceramic body having a metal matrix therein will be directly bonded to excess metal remaining in the reservoir.

Further improvements in metal matrix technology can be found in commonly owned and copending U.S. patent application Ser. No. 07/521,043, filed May 9, 1990, which is a continuation-in-part application of U.S.

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of non-infiltratable material, etc.). Specifically, an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere are in communication with the filler material or preform at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler material or preform up to the shape defining means.

The shape defining means is not spontaneously infiltrated by the molten matrix metal and accordingly, the 10 configuration of the shape defining means, when removed, is substantially completely inversely replicated in the formed metal matrix composite body. The shape defining means may be utilized to provide channels through at least a portion of the formed metal matrix composite body. Alternatively, the shape defining means may be utilized to define an interior cavity in a metal matrix composite body. Accordingly, any channel(s) and cavity, simple or complex (e.g., a network of passageways or a complicated internal shape) of any desired configuration, size, and location, can be formed within a metal matrix composite body by practicing the teachings of the present invention. In a first preferred embodiment of the invention, a shape defining means comprising a mandrel, which is capable of surviving the processing conditions associated with the spontaneous infiltration process, is placed into a suitable vessel. A filler material is thereafter placed around the mandrel to form either a loose bed of filler or the filler material can be processed to become a self-supporting body of filler material (i.e., a preform). Molten matrix metal is then induced to spontaneously infiltrate the filler material or preform up to the shaped mandrel. The mandrel can then be removed, either at the processing temperature or at a temperature above or below the processing temperature, depending upon the composition and shape of the mandrel and the composition and shape of the metal matrix composite body. Suitable mandrels for use in the present invention include materials which themselves may not be capable of surviving the spontaneous infiltration process, but which can be coated by a material which is capable of surviving the spontaneous infiltration process. Such materials include, for example, materials which also function as barrier materials. Accordingly, the mandrel material may itself not be capable of surviving the spontaneous infiltration process, but, if coated by any suitable means, could function as a desirable mandrel. Moreover, if such a mandrel has been coated, either the coating or the mandrel itself should be capable of being easily removed by some step or combinations of steps. For example, if graphite was utilized as a mandrel to form an internal shape, once spontaneous infiltration has occurred, the graphite mandrel could be oxidized (e.g., by heating to a high temperature in an oxygen environment) and thereby removed from the formed metal matrix composite body. A mandrel can also be constructed of a material which is capable of being grit or air blasted away. Moreover, the composition of the mandrel could be selected so that the mandrel was removed by exposure to an appropriate leaching solution (e.g., acid, base, etc.). Still further, if the mandrel was of a simple shape and made of a material which did not interact chemically with any of the materials utilized in the spontaneous infiltration process, the mandrel could be physically removed from the metal matrix composite body by an exertion of pressure on the mandrel (e.g., pushing a graphite pin out of a formed metal matrix composite body).

patent application Ser. No. 07/484,753, filed Feb. 23, 15 1990, which is a continuation-in-part application of U.S. patent application Ser. No. 07/432,661, filed Nov. 7, 1989 (now abandoned), which is a continuation-in-part application of U.S. patent application Ser. No. 07/416,327, filed Oct. 6, 1989 (now abandoned), which 20 is a continuation-in-part application of U.S. patent application Ser. No. 07/349,590, filed May 9, 1989 (now abandoned), which in turn is a continuation-in-part application of U.S. patent application Ser. No. 07/269,311, filed Nov. 10, 1988 (now abandoned), all of 25 which were filed in the names of Michael K. Aghajanian et al. and all of which are entitled "A Method of Forming Metal Matrix Composite Bodies By A Spontaneous Infiltration Process, and Products Produced Therefrom" (an EPO application corresponding to U.S. 30) application Ser. No. 07/416,327 was published in the EPO on Jun. 27, 1990, as Publication No. 0 375 588). According to these Aghajanian et al. applications, spontaneous infiltration of a matrix metal into a permeable mass of filler material or preform is achieved by use of 35 an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere which are in communication with the filler material or preform, at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler 40 material or preform. Aghajanian et al. disclose a number of matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems which exhibit spontaneous infiltration. Specifically, Aghajanian et al. disclose that spontaneous infiltration behavior has been observed in 45 the aluminum/magnesium/nitrogen system; the aluminum/strontium/nitrogen system; the aluminum/zinc-/oxygen system; and the aluminum/calcium/nitrogen system. However, it is clear from the disclosure set forth in the Aghajanian et al. applications that the spon-50 taneous infiltration behavior should occur in other matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems. Each of the above-discussed Commonly Owned Metal Matrix Patents and Patent Applications describes 55 methods for the production of metal matrix composite bodies and novel metal matrix composite bodies which are produced therefrom. The entire disclosures of all of the foregoing Commonly Owned Metal Matrix Patents and Patent Applications are expressly incorporated 60 herein by reference.

SUMMARY OF THE INVENTION

A metal matrix composite body is produced by spontaneously infiltrating a molten matrix metal into a per- 65 meable mass of filler material or a preform wherein at least a portion of the filler material or preform contains therein a shape defining means (e.g., a mandrel, a mass

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The mandrel can be of any desired shape so as to form virtually any internal shape in a metal matrix composite body. However, the combination of mandrel composition, mandrel shape and desired removal process all must be taken into consideration when choosing materials for use as mandrels. Moreover, the mandrel should not adversely affect the spontaneous infiltration process. Additionally, removal of the mandrel should not adversely affect the formed metal matrix composite body. 10

In another preferred embodiment, the shape defining means comprises a bed or mass of particles which is not capable of being spontaneously infiltrated by the matrix metal under the given set of processing conditions. A bed or mass of particles (e.g., particulate alumina) 15 which does not incorporate an infiltration enhancer and/or an infiltration enhancer precursor may be placed into a cavity-containing preform which is to be spontaneously infiltrated with matrix metal. When the preform is contacted and spontaneously infiltrated by the 20 molten matrix metal, the shape defining means (or particles) define the geometry of the interior cavity of the metal matrix composite by preventing molten matrix metal from infiltrating into the particles. The non-infiltrated material may be removed by any physical, me- 25 chanical or chemical means including air blasting, grit blasting, leaching, shaking, etc. In each of the above-discussed embodiments, a precursor to an infiltration enhancer may be supplied to at least one of a filler material or preform, and/or a matrix 30 metal and/or an infiltrating atmosphere. The supplied infiltration enhancer precursor may thereafter react with at least one of the filler material or preform, and-/or the matrix metal and/or the infiltrating atmosphere to produce infiltration enhancer in at least a portion of, 35 or on, the filler material or preform. Ultimately, at least during the spontaneous infiltration, infiltration enhancer should be in contact with at least a portion of the filler material or preform. In another preferred embodiment of the invention, 40 rather than supplying an infiltration enhancer precursor, an infiltration enhancer may be supplied directly to at least one of the preform, and/or matrix metal, and/or infiltrating atmosphere. Ultimately, at least during the spontaneous infiltration, the infiltration enhancer 45 should be in contact with at least a portion of the filler material or preform. This application discusses various examples of matrix metals, which at some point during the formation of a metal matrix composite, are contacted with an infiltra- 50 tion enhancer precursor, in the presence of an infiltrating atmosphere. Thus, various references will be made to particular matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems which exhibit spontaneous infiltration. However, it is conceivable that 55 many other matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems other than those discussed in this application may behave in a manner similar to the systems discussed above herein. Specifically, spontaneous infiltration behavior has been ob- 60 served in the aluminum/magnesium/nitrogen system; the aluminum/strontium/nitrogen system; the aluminum/zinc/oxygen system; and the aluminum/calcium/nitrogen system. Accordingly, even though this application discusses only those systems referred to above 65 herein (with particular emphasis being placed upon the aluminum/magnesium/nitrogen system), it should be understood that other matrix metal/infiltration en-

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hancer precursor/infiltrating atmosphere systems may behave in a similar manner.

In a preferred embodiment for achieving spontaneous infiltration into a permeable mass of filler material or a preform containing a mandrel, molten matrix metal is contacted with the preform or filler material. The preform or filler material may have admixed therewith, and/or at some point during the process, be exposed to, an infiltration enhancer precursor. Moreover, in a pre-10 ferred embodiment, the molten matrix metal and/or preform or filler material communicate with an infiltrating atmosphere for at least a portion of the process. In another preferred embodiment, the matrix metal and/or preform or filler material communicate with an infiltrating atmosphere for substantially all of the process. The preform or filler material will be spontaneously infiltrated by molten matrix metal up to the surface of the mandrel, and the extent or rate of spontaneous infiltration and formation of metal matrix composite material will vary with a given set of processing conditions including, for example, the concentration of infiltration enhancer precursor provided to the system (e.g., in the molten matrix alloy and/or in the filler material or preform and/or in the infiltrating atmosphere), the size and/or composition of the filler material, the size and-/or composition of particles in the preform, the available porosity for infiltration into the preform or filler material, the time permitted for infiltration to occur, and/or the temperature at which infiltration occurs. Spontaneous infiltration typically occurs to an extent sufficient to embed substantially completely the preform or filler material. Moreover, by varying the composition of the matrix metal and/or the processing conditions, the physical and mechanical properties of the formed metal matrix composite bodies may be engineered to any particular application or need. Further, by subjecting a formed metal matrix composite body to a post treatment process (e.g., directional solidification, heat treatment, etc.) the mechanical and/or physical properties may be further engineered to meet any particular application or need. Still further, by controlling the processing conditions during the formation of a metal matrix composite the nitrogen content of the formed metal matrix composite may be tailored to meet a wide range of industrial applications. Moreover, by controlling the composition and/or size (e.g., particle diameter) and/or geometry of the filler material or the material comprising the preform, the physical and/or mechanical properties of the formed metal matrix composite can be controlled or engineered to meet any number of industrial needs. For example, it has been discovered that wear resistance of the metal matrix composite can be increased by increasing the size of the filler material (e.g., increasing the average diameter of the filler material particles), given that the wear resistance of filler material is higher than that of the matrix metal. However, strength and/or toughness may tend to increase with decreasing filler size. Further, the thermal expansion coefficient of the metal matrix composite may decrease with increasing filler loading, given that the coefficient of thermal expansion of the filler is lower than the coefficient of thermal expansion of the matrix metal. Still further, the mechanical and/or physical properties (e.g., density, elastic and/or specific modulus, strength and/or specific strength, etc.) of a formed metal matrix composite body may be tailored depending on the loading of the

filler material in the loose mass or in the preform. For example, by providing a loose mass or preform comprising a mixture of filler particles of varying sizes and/or shapes, wherein the density of the filler is greater than that of the matrix metal, a higher filler loading, due to 5 enhanced packing of the filler material, may be achieved, thereby resulting in a metal matrix composite body with an increased density. By utilizing the teachings of the present invention, the volume percent of filler material or preform which can be infiltrated can 10 vary over a wide range. The lower volume percent of filler that can be infiltrated is limited primarily by the ability to form a porous filler material or preform, (e.g., about 10 volume percent); whereas the higher volume percent of filler or preform that can be infiltrated is 15 limited primarily by the ability to form a dense filler material or preform with at least some interconnected porosity (e.g., about 95 volume percent). Accordingly, by practicing any of the above teachings, alone or in combination, a metal matrix composite can be engi- 20 neered to contain a desired combination of properties.

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"Carcass" or "Carcass of Matrix Metal", as used herein, refers to any of the original body of matrix metal remaining which has not been consumed during formation of the metal matrix composite body, and typically, if allowed to cool, remains in at least partial contact with the metal matrix composite body which has been formed. It should be understood that the carcass may also include a second or foreign metal therein.

"Channel", as used herein, refers to an unfilled space, cavity, passageway, or the like, not necessarily of uniform dimension, within a metal matrix composite, and is not limited to a tubular configuration.

"Filler", as used herein, is intended to include either single constituents or mixtures of constituents which are

DEFINITIONS

"Aluminum", as used herein, means and includes essentially pure metal (e.g., a relatively pure, commer- 25 cially available unalloyed aluminum) or other grades of metal and metal alloys such as the commercially available metals having impurities and/or alloying constituents such as iron, silicon, copper, magnesium, manganese, chromium, zinc, etc., therein. An aluminum alloy 30 for purposes of this definition is an alloy or intermetallic compound in which aluminum is the major constituent. "Balance Non-Oridizing Gas" as used herein means

"Balance Non-Oxidizing Gas", as used herein, means that any gas present in addition to the primary gas comprising the infiltrating atmosphere, is either an inert gas 35 or a reducing gas which is substantially non-reactive with the matrix metal under the process conditions. Any oxidizing gas which may be present as an impurity in the gas(es) used should be insufficient to oxidize the matrix metal to any substantial extent under the process 40 conditions. "Barrier" or "barrier means", as used herein, means any suitable means which interferes, inhibits, prevents or terminates the migration, movement, or the like, of molten matrix metal beyond a surface boundary of a 45 permeable mass of filler material or preform, where such surface boundary is defined by said barrier means. Suitable barrier means may be any such material, compound, element, composition, or the like, which, under the process conditions, maintains some integrity and is 50 not substantially volatile (i.e., the barrier material does not volatilize to such an extent that it is rendered nonfunctional as a barrier). Further, suitable "barrier means" includes materials which are substantially non-wettable by the migrating 55 molten matrix metal under the process conditions employed. A barrier of this type appears to exhibit substantially little or no affinity for the molten matrix metal, and movement beyond the defined surface boundary of the mass of filler material or preform is prevented or 60 inhibited by the barrier means. The barrier reduces any final machining or grinding that may be required and defines at least a portion of the surface of the resulting metal matrix composite product. The barrier may in certain cases be permeable or porous, or rendered per- 65 meable by, for example, drilling holes or puncturing the barrier, to permit gas to contact the molten matrix metal, etc.

substantially nonreactive with and/or of limited solubility in the matrix metal and may be single or multi-phase. Fillers may be provided in a wide variety of forms and sizes, such as powders, flakes, platelets, microspheres, whiskers, bubbles, fibers, particulates, fiber mats, chopped fibers, spheres, pellets, tubules, refractory cloths, etc., and may be either dense or porous. "Filler" may also include ceramic fillers, such as alumina or silicon carbide as fibers, chopped fibers, particulates, whiskers, bubbles, spheres, fiber mats, or the like, and ceramic-coated fillers such as carbon fibers coated with alumina or silicon carbide to protect the carbon from attack, for example, by a molten aluminum parent metal. Fillers may also include metals.

"*Hot-Topping*", as used herein, refers to the placement of a substance on one end (the "topping" end) of an at least partially formed metal matrix composite which reacts exothermically with at least one of the matrix metal and/or filler material and/or with another material supplied to the topping end. This exothermic reaction should provide sufficient heat to maintain the matrix metal at the topping end in a molten state while the balance of the matrix metal in the composite cools to solidification temperature. "Infiltrating Atmosphere", as used herein, means that atmosphere which is present which interacts with the matrix metal and/or preform (or filler material) and/or infiltration enhancer precursor and/or infiltration enhancer and permits or enhances spontaneous infiltration of the matrix metal. "Infiltration Enhancer", as used herein, means a material which promotes or assists in the spontaneous infiltration of a matrix metal into a filler material or preform. An infiltration enhancer may be formed from, for example, (1) a reaction of an infiltration enhancer precursor with an infiltrating atmosphere to form a gaseous species and/or (2) a reaction product of the infiltration enhancer precursor and the infiltrating atmosphere and-/or (3) a reaction product of the infiltration enhancer precursor and the filler material or preform. Moreover, the infiltration enhancer may be supplied directly to at least one of the preform, and/or matrix metal, and/or infiltrating atmosphere and function in a substantially similar manner to an infiltration enhancer which has formed as a reaction between an infiltration enhancer precursor and another species. Ultimately, at least during the spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform to achieve spontaneous infiltration, and the infiltration enhancer may be at least partially reducible by the matrix metal. "Infiltration Enhancer Precursor" or "Precursor to the Infiltration Enhancer", as used herein, means a material which when used in combination with (1) the matrix

metal, (2) the preform or filler material and/or (3) an infiltrating atmosphere forms an infiltration enhancer which induces or assists the matrix metal to spontaneously infiltrate the filler material or preform. Without wishing to be bound by any particular theory or expla-5 nation, it appears as though it may be necessary for the precursor to the infiltration enhancer to be capable of being positioned, located or transportable to a location which permits the infiltration enhancer precursor to interact with the infiltrating atmosphere and/or the 10 preform or filler material and/or matrix metal. For example, in some matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems, it is desirable for the infiltration enhancer precursor to volatilize at, near, or in some cases, even somewhat above the 15 temperature at which the matrix metal becomes molten. Such volatilization may lead to: (1) a reaction of the infiltration enhancer precursor with the infiltrating atmosphere to form a gaseous species which enhances wetting of the filler material or preform by the matrix 20 metal; and/or (2) a reaction of the infiltration enhancer precursor with the infiltrating atmosphere to form a solid, liquid or gaseous infiltration enhancer in at least a portion of the filler material or preform which enhances wetting; and/or (3) a reaction of the infiltration en- 25hancer precursor within the filler material or preform which forms a solid, liquid or gaseous infiltration enhancer in at least a portion of the filler material or preform which enhances wetting. "Matrix Metal" or "Matrix Metal Alloy", as used 30 herein, means that metal which is utilized to form a metal matrix composite body (e.g., before infiltration) and/or that metal which is intermingled with a filler material to form a metal matrix composite body (e.g., after infiltration). When a specified metal is mentioned 35 as the matrix metal, it should be understood that such matrix metal includes that metal as an essentially pure metal, a commercially available metal having impurities and/or alloying constituents therein, an intermetallic compound or an alloy in which that metal is the major 40 or predominant constituent. "Matrix Metal/Infiltration Enhancer Precursor/Infiltrating Atmosphere System" or "Spontaneous System", as used herein, refers to that combination of materials which exhibit spontaneous infiltration into a preform or 45 filler material. It should be understood that whenever a "/" appears between an exemplary matrix metal, infiltration enhancer precursor and infiltrating atmosphere that the "/" is used to designate a system or combination of materials which, when combined in a particular 50 manner, exhibits spontaneous infiltration into a preform or filler material. "Metal Matrix Composite" or "MMC", as used herein, means a material comprising a two- or three-dimensionally interconnected alloy or matrix metal which has 55 embedded a preform or filler material. The matrix metal may include various alloying elements to provide specifically desired mechanical and physical properties in the resulting composite. A Metal "Different" from the Matrix Metal means a 60 metal which does not contain, as a primary constituent, the same metal as the matrix metal (e.g., if the primary constituent of the matrix metal is aluminum, the "different" metal could have a primary constituent of, for 65 example, nickel). "Nonreactive Vessel for Housing Matrix Metal" means any vessel which can house or contain a filler material (or preform) and/or molten matrix metal under the

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process conditions and not react with the matrix and/or the infiltrating atmosphere and/or infiltration enhancer precursor and/or a filler material or preform in a manner which would be significantly detrimental to the spontaneous infiltration mechanism. The nonreactive vessel may be disposable and removable after the spontaneous infiltration of the molten matrix metal has been completed.

"Preform" or "Permeable Preform", as used herein, means a porous mass of filler or filler material which is manufactured with at least one surface boundary which essentially defines a boundary for infiltrating matrix metal, such mass retaining sufficient shape integrity and green strength to provide dimensional fidelity prior to being infiltrated by the matrix metal. The mass should be sufficiently porous to accommodate spontaneous infiltration of the matrix metal thereinto. A preform typically comprises a bonded array or arrangement of filler, either homogeneous or heterogeneous, and may be comprised of any suitable material (e.g., ceramic and/or metal particulates, powders, fibers, whiskers, etc., and any combination thereof). A preform may exist either singularly or as an assemblage. "Reservoir", as used herein, means a separate body of matrix metal positioned relative to a mass of filler or a preform so that, when the metal is molten, it may flow to replenish, or in some cases to initially provide and subsequently replenish, that portion, segment or source of matrix metal which is in contact with the filler or preform.

"Shape Defining Means", as used herein, means a material comprising a solid, particulate, fiber, etc., which is utilized to define a channel or cavity or series of channels or cavities within a metal matrix composite body. The shape defining means can comprise a refractory material which is capable of, or rendered capable of, surviving the spontaneous infiltration process and not adversely impacting the spontaneous infiltration process. The shape defining means may possess any desired shape or size, and should be made of or coated by a material which will not be spontaneously infiltrated under the processing conditions. "Spontaneous Infiltration", as used herein, means the infiltration of matrix metal into the permeable mass of filler or preform occurs without requirement for the application of pressure or vacuum (whether externally applied or internally created).

BRIEF DESCRIPTION OF THE FIGURES

The following Figures are provided to assist in understanding the invention, but are not intended to limit the scope of the invention. Similar reference numerals have been used wherever possible in each of the Figures to

denote like components, wherein:

FIGS. 1*a* and 1*b* show a schematic cross-sectional view of a lay-up utilized to form a metal matrix composite body according to Example 1;

FIG. 2 shows a schematic cross-sectional view of a lay-up utilized to form a metal matrix composite according to Example 2; and

FIG. 3 shows a schematic cross-sectional view of a lay-up utilized to form a metal matrix composite according to Example 3.

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DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

A metal matrix composite body is produced by spon-5 taneously infiltrating a molten matrix metal into a permeable mass of filler material or a preform wherein at least a portion of the filler material or preform contains therein a shape defining means (e.g., a mandrel, a mass of non-infiltratable material, etc.). Specifically, an infil- 10 tration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere are in communication with the filler material or preform at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler material or 15 preform up to the shape defining means. The shape defining means is not spontaneously infiltrated by the molten matrix metal and accordingly, the configuration of the shape defining means, when removed, is substantially completely inversely replicated 20 in the formed metal matrix composite body. The shape defining means may be utilized to provide channels through at least a portion of the formed metal matrix composite body. Alternatively, the shape defining means may be utilized to define an interior cavity in a 25 metal matrix composite body. Accordingly, any channel(s) or cavity, simple or complex (e.g., a network of passageways or a complicated internal shape) of any desired configuration, size, and location, can be formed within a metal matrix composite body by practicing the 30 teachings of the present invention.

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moved by exposure to an appropriate leaching solution (e.g., acid, base, etc.). Still further, if the mandrel was of a simple shape and made of a material which did not interact chemically with any of the materials utilized in the spontaneous infiltration process, the mandrel could be physically removed from the metal matrix composite body by an exertion of pressure on the mandrel (e.g., pushing a graphite pin out of a formed metal matrix composite body).

The mandrel can be of any desired shape so as to form virtually any internal shaped in a metal matrix composite body. However, the combination of mandrel composition, mandrel shape and desired removal process all must be taken into consideration when choosing materials for use as mandrels. Moreover, the mandrel should not adversely affect the spontaneous infiltration process. Additionally, removal of the mandrel should not adversely effect the formed metal matrix composite body. In another preferred embodiment, the shape defining means comprises a bed or mass of particles which is not capable of being spontaneously infiltrated by the matrix metal under the given set of processing conditions. A bed or mass of particles (e.g., particulate alumina) which does not incorporate an infiltration enhancer and/or an infiltration enhancer precursor may be placed into a cavity-containing preform which is to be spontaneously infiltrated with matrix metal. When the preform is contacted and spontaneously infiltrated by the molten matrix metal, the shape defining means (or particles) define the geometry of the interior cavity of the metal matrix composite by preventing molten matrix metal from infiltrating into the particles. The non-infiltrated material may be removed by any physical, mechanical or chemical means including air blasting, grit blasting, leaking, shaking, etc. In regard to each of the above-discussed embodiments and without wishing to be bound by any particular theory or explanation, when an infiltration enhancer precursor is utilized in combination with at least one of the matrix metal, and/or filler material or preform and-/or infiltrating atmosphere, the infiltration enhancer precursor may react to form an infiltration enhancer which induces or assists molten matrix metal to spontaneously infiltrate a filler material or preform. Moreover, it appears as though it may be necessary for the precursor to the infiltration enhancer to be capable of being positioned, located or transportable to a location which permits the infiltration enhancer precursor to interact with at least one of the infiltrating atmosphere, and/or the preform or filler material, and/or molten matrix metal. For example, in some matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems, it is desirable for the infiltration enhancer precursor to volatilize at, near, or in some cases, even somewhat above the temperature at which the matrix metal becomes molten. Such volatilization may lead to: (1) a reaction of the infiltration enhancer precursor with the infiltrating atmosphere to form a gaseous species which enhances wetting of the filler material or preform by the matrix metal; and/or (2) a reaction of the infiltration enhancer precursor with the infiltrating atmosphere to form a solid, liquid or gaseous infiltration enhancer in at least a portion of the filler material or preform which enhances wetting; and/or (3) a reaction of the infiltration enhancer precursor within the filler material or preform which forms a solid, liquid or gaseous infiltra-

In a first preferred embodiment of the invention, a shape defining means comprising a mandrel, which is capable of surviving the processing conditions associated with the spontaneous infiltration process, is placed 35 into a suitable vessel. A filler material is thereafter placed around the mandrel to form either a loose bed of filler or the filler material can be processed to become a self-supporting body of filler material (i.e., a preform). Molten matrix metal is then induced to spontaneously 40 infiltrate the filler material or preform up to the shaped mandrel. The mandrel can then be removed, either at the processing temperature or at a temperature above or below the processing temperature, depending upon the composition and shape of the mandrel and the composi- 45 tion and shape of the metal matrix composite body. Suitable mandrels for use in the present invention include materials which themselves may not be capable of surviving the spontaneous infiltration process, but which can be coated by a material which is capable of 50 surviving the spontaneous infiltration process. Such materials include, for example, materials which also function as barrier materials. Accordingly, the mandrel material may itself not be capable of surviving the spontaneous infiltration process, but, if coated by any suit- 55 able means, could function as a desirable mandrel. Moreover, if such a mandrel has been coated, either the coating or the mandrel itself should be capable of being easily removed by some step or combinations of steps. For example, if graphite was utilized as a mandrel to 60 form an internal shape, once spontaneous infiltration has occurred, the graphite mandrel could be oxidized (e.g., by heating to a high temperature in an oxygen environment) and thereby removed from the formed metal matrix composite body. A mandrel can also be 65 constructed of a material which is capable of being grit or air blasted away. Moreover, the composition of the mandrel could be selected so that the mandrel was re-

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tion enhancer in at least a portion of the filler material or preform which enhances wetting.

Thus, for example, if an infiltration enhancer precursor is included or combined with, at least at some point during the process, molten matrix metal, it is possible 5 that the infiltration enhancer may volatilize from the molten matrix metal and react with at least one of the filler material or preform and/or the infiltrating atmosphere. Such reaction may result in the formation of a solid species, if such solid species is stable at the infiltra-10 tion temperature, said solid species being capable of being deposited on at least a portion of the filler material or preform as, for example, a coating. Moreover, it is conceivable that such solid species may be present as a discernable solid within at least a portion of the preform 15 or filler material. If such a solid species is formed, molten matrix metal may have a tendency to react (e.g., the molten matrix metal may reduce the formed solid species) such that infiltration enhancer precursor may become associated with (e.g., dissolved in or alloyed with) 20 the molten matrix metal. Accordingly, additional infiltration enhancer precursor may then be available to volatilize and react with another species (e.g., the filler material or preform and/or infiltrating atmosphere) and again form a similar solid species. It is conceivable that 25 a continuous process of conversion of infiltration enhancer precursor to infiltration enhancer followed by a reduction reaction of the infiltration enhancer with molten matrix metal to again form additional infiltration enhancer, and so on, may occur, until the result 30 achieved is a spontaneously infiltrated metal matrix composite.

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be contacted with molten aluminum matrix metal and spontaneously infiltrated.

Moreover, rather than supplying an infiltration enhancer precursor, an infiltration enhancer may be supplied directly to at least one of the preform or filler material, and/or matrix metal, and/or infiltrating atmosphere. Ultimately, at least during the spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform.

Under the conditions employed in the method of the present invention, in the case of an aluminum/magnesium/nitrogen spontaneous infiltration system, the preform or filler material should be sufficiently permeable to permit the nitrogen-containing gas to penetrate or permeate the filler material or preform at some point during the process and/or contact the molten matrix metal. Moreover, the permeable filler material or preform can accommodate infiltration of the molten matrix metal, thereby causing the nitrogen-permeated preform to be infiltrated spontaneously with molten matrix metal to form a metal matrix composite body and/or cause the nitrogen to react with an infiltration enhancer precursor to form infiltration enhancer in the filler material or preform and thereby result in spontaneous infiltration. The extent of spontaneous infiltration and formation of the metal matrix composite will vary with a given set of process conditions, including magnesium content of the aluminum alloy, magnesium content of the preform or filler material, amount of magnesium nitride in the preform or filler material, the presence of additional alloying elements (e.g., silicon, iron, copper, manganese, chromium, zinc, and the like), average size of the filler material (e.g., particle diameter) comprising the preform or the filler material, surface condition and type of filler material or preform, nitrogen concentration of the infiltrating atmosphere, time permitted for infiltration and temperature at which infiltration occurs. For example, for infiltration of the molten aluminum matrix metal to occur spontaneously, the aluminum can be alloyed with at least about 1 percent by weight, and preferably at least about 3 percent by weight, magnesium (which functions as the infiltration enhancer precursor), based on alloy weight. Auxiliary alloying elements, as discussed above, may also be included in the matrix metal to tailor specific properties thereof. Additionally, the auxiliary alloying elements may affect the minimum amount of magnesium required in the matrix aluminum metal to result in spontaneous infiltration of the filler material or preform. Loss of magnesium from the spontaneous system due to, for example, volatilization should not occur to such an extent that no magnesium was present to form infiltration enhancer. Thus, it is desirable to utilize a sufficient amount of initial alloying elements to assure that spontaneous infiltration will not be adversely affected by volatilization. Still further, the presence of magnesium in both of the preform (or filler material) and matrix metal or the preform (or filler material) alone may result in a reduction in required amount of magnesium to achieve spontaneous infiltration (discussed in greater detail later herein). 60 The volume percent of nitrogen in the infiltrating atmosphere also affects formation rates of the metal matrix composite body. Specifically, if less than about 10 volume percent of nitrogen is present in the atmosphere, very slow or little spontaneous infiltration will occur. It has been discovered that it is preferable for at least about 50 volume percent of nitrogen to be present in the atmosphere, thereby resulting in, for example,

In order to effect spontaneous infiltration of the matrix metal into the filler material or preform, an infiltration enhancer should be provided to the spontaneous 35 system. An infiltration enhancer could be formed from an infiltration enhancer precursor which may be provided (1) in the matrix metal; and/or (2) in the filler $\frac{1}{2}$ material or preform; and/or (3) from the infiltrating atmosphere; and/or (4) from an external source into the 40 spontaneous system. Moreover, rather than supplying an infiltration enhancer precursor, an infiltration enhancer may be supplied directly to at least one of the filler material or preform, and/or matrix metal, and/or infiltrating atmosphere. Ultimately, at least during the 45 spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform. In another preferred embodiment of the invention, it is possible that the infiltration enhancer precursor can 50 be at least partially reacted with the infiltrating atmosphere such that the infiltration enhancer can be formed in at least a portion of the filler material or preform prior to or substantially contiguous with contacting the filler material or preform with the matrix metal (e.g., if 55 magnesium is the infiltration enhancer precursor and nitrogen was the infiltrating atmosphere, the infiltration enhancer may be magnesium nitride which would be located in at least a portion of the preform or filler material). An example of a matrix metal/infiltration enhancer precursor/infiltrating atmosphere system is the aluminum/magnesium/nitrogen system. Specifically, an aluminum matrix metal can be contained within a suitable refractory vessel which, under the process conditions, 65 does not adversely react with the aluminum matrix metal and/or the filler material when the aluminum is made molten. A filler material or preform can thereafter

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shorter infiltration times due to a much more rapid rate of infiltration. The infiltrating atmosphere (e.g., a nitrogen-containing gas) can be supplied directly to the filler material or preform and/or matrix metal, or it may be produced or result from a decomposition of a material. 5

The minimum magnesium content required for the molten matrix metal to infiltrate a filler material or preform depends on one or more variables such as the processing temperature, time, the presence of auxiliary alloying elements such as silicon or zinc, the nature of 10 the filler material, the location of the magnesium in one or more components of the spontaneous system, the nitrogen content of the atmosphere, and the rate at which the nitrogen atmosphere flows. Lower temperatures or shorter heating times can be used to obtain 15 complete infiltration as the magnesium content of the alloy and/or preform is increased. Also, for a given magnesium content, the addition of certain auxiliary alloying elements such as zinc permits the use of lower temperatures. For example, a magnesium content of the 20 matrix metal at the lower end of the operable range, e.g., from about 1 to 3 weight percent, may be used in conjunction with at least one of the following: an above-minimum processing temperature, a high nitrogen concentration, or one or more auxiliary alloying 25 elements. When no magnesium is added to the preform, alloys containing from about 3 to 5 weight percent magnesium are preferred on the basis of their general utility over a wide variety of process conditions, with at least about 5 percent being preferred when lower tem- 30 peratures and shorter times are employed. Magnesium contents in excess of about 10 percent by weight of the aluminum alloy may be employed to moderate the temperature conditions required for infiltration. The magnesium content may be reduced when used in conjunc- 35 tion with an auxiliary alloying element, but these elements serve an auxiliary function only and are used together with at least the above-specified minimum amount of magnesium. For example, there was substantially no infiltration of nominally pure aluminum al- 40 loyed only with 10 percent silicon at 1000° C. into a bedding of 500 mesh, 39 CRYSTOLON (R) (99 percent pure silicon carbide from Norton Co.). However, in the presence of magnesium, silicon has been found to promote the infiltration process. As a further example, the 45 amount of magnesium varies if it is supplied exclusively to the preform or filler material. It has been discovered that spontaneous infiltration will occur with a lesser weight percent of magnesium supplied to the spontaneous system when at least some of the total amount of 50 magnesium supplied is placed in the preform or filler material. It may be desirable for a lesser amount of magnesium to be provided in order to prevent the formation of undesirable intermetallics in the metal matrix composite body. In the case of a silicon carbide pre- 55 form, it has been discovered that when the preform is contacted with an aluminum matrix metal, the preform containing at least about 1% by weight magnesium and being in the presence of a substantially pure nitrogen atmosphere, the matrix metal spontaneously infiltrates 60 the preform. In the case of an alumina preform, the amount of magnesium required to achieve acceptable spontaneous infiltration is slightly higher. Specifically, it has been found that when an alumina preform is contacted with a similar aluminum matrix metal, at about 65 the same temperature as the aluminum that infiltrated into the silicon carbide preform, and in the presence of the same nitrogen atmosphere, at least about 3% by

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weight magnesium may be required to achieve similar spontaneous infiltration to that achieved in the silicon carbide preform discussed immediately above.

It is also noted that it is possible to supply to the spontaneous system infiltration enhancer precursor and-/or infiltration enhancer on a surface of the alloy and-/or on a surface of the preform or filler material and/or within the preform or filler material prior to infiltrating the matrix metal into the filler material or preform (i.e., it may not be necessary for the supplied infiltration enhancer or infiltration enhancer precursor to be alloyed with the matrix metal, but rather, simply supplied to the spontaneous system). For example, in the aluminum/magnesium/nitrogen system, if the magnesium is applied to a surface of the matrix metal it may be preferred that the surface should be the surface which is closest to, or preferably in contact with, the permeable mass of filler material or vice-versa; or such magnesium may be mixed into at least a portion of the preform or filler material. Still further, it is possible that some combination of surface application, alloying and placement of magnesium into at least a portion of the preform may be used. Such combination of applying infiltration enhancer(s) and/or infiltration enhancer precursor(s) may result in a decrease in the total weight percent of magnesium needed to promote infiltration of the matrix aluminum metal into the preform, as well as achieving lower temperatures at which infiltration can occur. Moreover, the amount of undesirable intermetallics formed due to the presence of magnesium may also be minimized. The use of one or more auxiliary alloying elements and the concentration of nitrogen in the surrounding gas also affects the extent of nitriding of the matrix metal at a given temperature. For example, auxiliary alloying elements such as zinc or iron included in the alloy, or placed on a surface of the alloy, may be used to reduce the infiltration temperature and thereby decrease the amount of nitride formation, whereas increasing the concentration of nitrogen in the gas may be used to promote nitride formation. The concentration of magnesium in the alloy, and/or placed onto a surface of the alloy, and/or combined in the filler or preform material, also tends to affect the extent of infiltration at a given temperature. Consequently, in some cases where little or no magnesium is contacted directly with the preform or filler material, it may be preferred that at least about three weight percent magnesium be included in the alloy. Alloy contents of less than this amount, such as one weight percent magnesium, may require higher process temperatures or an auxiliary alloying element for infiltration. The temperature required to effect the spontaneous infiltration process of this invention may be lower: (1) when the magnesium content of the alloy alone is increased, e.g., to at least about 5 weight percent; and/or (2) when alloying constituents are mixed with the permeable mass of filler material or preform; and/or (3) when another element such as zinc or iron is present in the aluminum alloy. The temperature also may vary with different filler materials. In general, in the aluminum/magnesium/nitrogen system spontaneous and progressive infiltration will occur at a process temperature of at least about 675° C., and preferably a process temperature of at least about 750° C.-800° C. Temperatures generally in excess of 1200° C. do not appear to benefit the process, and a particularly useful temperature range has been found to be from about 675° C. to about 1000°

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C. However, as a general rule, the spontaneous infiltration temperature is a temperature which is above the melting point of the matrix metal but below the volatilization temperature of the matrix metal. Moreover, the spontaneous infiltration temperature should be below 5 the melting point of the filler material. Still further, as temperature is increased, the tendency to form a reaction product between the matrix metal and infiltrating atmosphere increases (e.g., in the case of aluminum matrix metal and a nitrogen infiltrating atmosphere, 10 aluminum nitride may be formed). Such reaction product may be desirable or undesirable based upon the intended application of the metal matrix composite body. Additionally, electric resistance heating is typically used to achieve the infiltrating temperatures. 15 However, any heating means which can cause the matrix metal to become molten and does not adversely affect spontaneous infiltration is acceptable for use with the invention. In the present method, for example, a permeable filler 20 material or preform comes into contact with molten aluminum in the presence of, at least sometime during the process, a nitrogen-containing gas. The nitrogencontaining gas may be supplied by maintaining a continuous flow of gas into contact with at least one of the 25 filler material or preform and/or molten aluminum matrix metal. Although the flow rate of the nitrogen-containing gas is not critical, it is preferred that the flow rate be sufficient to compensate for any nitrogen lost from the atmosphere due to any nitride formation, and 30 also to prevent or inhibit the incursion of air which can have an oxidizing effect on the molten metal.

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crushed alumina bodies made by the method disclosed in copending and commonly owned application Ser. No. 819,397, entitled "Composite Ceramic Articles and Methods of Making Same", in the names of Marc S. Newkirk et al., also exhibit desirable infiltration properties relative to commercially available alumina products. The subject matter of each of the issued Patent and Copending Patent Application is herein expressly incorporated by reference. Thus, it has been discovered that complete infiltration of a permeable mass of ceramic material can occur at lower infiltration temperatures and/or lower infiltration times by utilizing a crushed or comminuted body produced by the method of the aforementioned U.S. Patent and Patent Application. The size, shape, chemistry and volume percent of the filler material (or preform) can be any that may be required to achieve the properties desired in the composite. Thus, the filler material may be in the form of particles, whiskers, platelets or fibers since infiltration is not restricted by the shape of the filler material. Other shapes such as spheres, tubules, pellets, refractory fiber cloth, and the like may be employed. In addition, the size of the filler material does not limit infiltration, although a higher temperature or longer time period may be needed for complete infiltration of a mass of smaller particles than for larger particles or vice-versa depending on the particular reaction conditions. Average particle diameters as small as a micron or less to about 1100 microns or more can be successfully utilized in the present invention, with a range of about 2 microns through about 1000 microns being preferred for a vast majority of commercial applications. Further, the mass of filler material (or preform) to be infiltrated should be permeable (i.e., contain at least some interconnected porosity to render it permeable to molten matrix metal and/or to the infiltrating atmosphere). Moreover, by controlling the size (e.g., particle diameter) and/or geometry and-/or composition of the filler material or the material comprising the preform, the physical and mechanical properties of the formed metal matrix composite can be controlled or engineered to meet any number of industrial needs. For example, wear resistance of the metal matrix composite can be increased by increasing the size of the filler material (e.g., increasing the average diameter of the filler material particles) given that the filler material has a higher wear resistance than the matrix metal. However, strength and/or toughness may tend to increase with decreasing filler size. Further, the thermal expansion coefficient of the metal matrix composite may decrease with increasing filler loading, given that the coefficient of thermal expansion of the filler is lower than the coefficient of thermal expansion of the matrix metal. Still further, the mechanical and/or physical properties (e.g., density, coefficient of thermal expansion, elastic and/or specific modulus, strength and/or specific strength, etc.) of a formed metal matrix composite body may be tailored depending on the loading of the filler material in the loose mass or in the preform. For example, by providing a loose mass or preform comprising a mixture of filler particles of varying sizes and/or shapes, wherein the density of the filler is greater than that of the matrix metal, a higher filler loading, due to enhanced packing of the filler materials, may be achieved, thereby resulting in a metal matrix composite body with an increased density. By utilizing the teachings of the present invention, the volume percent of filler material or preform which can be infiltrated can vary over a wide range. The lower volume

The method of forming a metal matrix composite is applicable to a wide variety of filler materials, and the choice of filler materials will depend on such factors as 35 the matrix alloy, the process conditions, the reactivity of the molten matrix alloy with the filler material, and the properties sought for the final composite product. For example, when aluminum is the matrix metal, suitable filler materials include (a) oxides, e.g. alumina, 40 magnesia, zirconia; (b) carbides, e.g. silicon carbide; (c) borides, e.g. aluminum dodecaboride, titanium diboride, and (d) nitrides, e.g. aluminum nitride, and (e) mixtures thereof. If there is a tendency for the filler material to react with the molten aluminum matrix metal, this 45 might be accommodated by minimizing the infiltration time and temperature or by providing a non-reactive coating on the filler. The filler material may comprise a substrate, such as carbon or other nonceramic material, bearing a ceramic coating to protect the substrate from 50 attack or degradation. Suitable ceramic coatings include oxides, carbides, borides and nitrides. Ceramics which are preferred for use in the present method include alumina and silicon carbide in the form of particles, platelets, whiskers and fibers. The fibers can be 55 discontinuous (in chopped form) or in the form of continuous filament, such as multifilament tows. Further,

the filler material or preform may be homogeneous or heterogeneous.

It also has been discovered that certain filler materials 60 exhibit enhanced infiltration relative to filler materials having a similar chemical composition. For example, crushed alumina bodies made by the method disclosed in U.S. Pat. No. 4,713,360, entitled "Novel Ceramic Materials and Methods of Making Same", which issued 65 on Dec. 15, 1987, in the names of Marc S. Newkirk et al., exhibit desirable infiltration properties relative to commercially available alumina products. Moreover,

percent of filler that can be infiltrated is limited primarily by the ability to form a porous filler material or preform, (e.g., about 10 volume percent); whereas the higher volume percent of filler or preform that can be infiltrated is limited primarily by the ability to form a 5 dense filler material or preform with at least some interconnected porosity (e.g., about 95 volume percent). Accordingly, by practicing any of the above teachings, alone or in combination, a metal matrix composite can be engineered to contain a desired combination of prop-10 erties.

The method of forming metal matrix composites according to the present invention, not being dependent on the use of pressure to force or squeeze molten matrix

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It is therefore possible to tailor the constituency of the metal matrix during formation of the composite to impart certain characteristics to the resulting product. For a given system, the process conditions can be selected to control the nitride formation. A composite product containing an aluminum nitride phase will exhibit certain properties which can be favorable to, or improve the performance of, the product. Further, the temperature range for spontaneous infiltration with an aluminum alloy may vary with the ceramic material used. In the case of alumina as the filler material, the temperature for infiltration should preferably not exceed about 1000° C. if it is desired that the ductility of the matrix not be reduced by the significant formation of nitride. However, temperatures exceeding 1000° C. may be employed if it is desired to produce a composite with a less ductile and stiffer matrix. To infiltrate silicon carbide, higher temperatures of about 1200° C. may be employed since the aluminum alloy nitrides to a lesser extent, relative to the use of alumina as filler, when silicon carbide is employed as a filler material. Further, the constituency of the matrix metal within the metal matrix composite and defects, for example, porosity, may be modified by controlling the cooling rate of the metal matrix composite. For example, the metal matrix composite may be directionally solidified by any number of techniques including: placing the container holding the metal matrix composite upon a chill plate; and/or selectively placing insulating materials about the container. Further, the constituency of the metal matrix may be modified after formation of the metal matrix composite. For example, exposure of the formed metal matrix composite to a heat treatment may improve the tensile strength of the metal matrix composite. (The standard test for tensile strength is ASTM-D3552-77 (reapproved 1982).)

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metal into a preform or a mass of filler material, permits the production of substantially uniform metal matrix composites having a high volume fraction of filler material and low porosity. Higher volume fractions of filler material may be achieved by using a lower porosity initial mass of filler material. Higher volume fractions also may be achieved if the mass of filler is compacted or otherwise densified provided that the mass is not converted into either a compact with closed cell porosity or into a fully dense structure that would prevent 25 infiltration by the molten alloy. Specifically, volume fractions on the order of about 60 to 80 volume percent can be achieved by methods such as vibrational packing, controlling particle size distribution, etc. However, alternative techniques can be utilized to achieve even 30 higher volume fractions of filler. Volume fractions of filler on the order of 40 to 50 percent are preferred for thermo-forming in accordance with the present invention. At such volume fractions, the infiltrated composite maintains or substantially maintains its shape, thereby 35 facilitating secondary processing. Higher or lower particle loadings or volume fractions could be used, however, depending on the desired final composite loading after thermo-forming. Moreover, methods for reducing particle loadings can be employed in connection with 40the thermo-forming processes of the present invention to achieve lower particle loadings. It has been observed that for aluminum infiltration and matrix formation around a ceramic filler, wetting of the ceramic filler by the aluminum matrix metal may be $_{45}$ an important part of the infiltration mechanism. Further, the wetting of the filler by molten matrix metal may permit a uniform dispersion of the filler throughout the formed metal matrix composite and improve the bonding of the filler to the matrix metal. Moreover, at 50 low processing temperatures, a negligible or minimal amount of metal nitriding occurs resulting in a minimal discontinuous phase of aluminum nitride dispersed in the metal matrix. However, as the upper end of the temperature range is approached, nitridation of the 55 metal is more likely to occur. Thus, the amount of the nitride phase in the metal matrix can be controlled by varying the processing temperature at which infiltration occurs. The specific process temperature at which nitride formation becomes more pronounced also varies 60 with such factors as the matrix aluminum alloy used and its quantity relative to the volume of filler or preform, the filler material to be infiltrated, and the nitrogen concentration of the infiltrating atmosphere. For example, the extent of aluminum nitride formation at a given 65 process temperature is believed to increase as the ability of the alloy to wet the filler decreases and as the nitrogen concentration of the atmosphere increases.

For example, a desirable heat treatment for a metal matrix composite containing a 520.0 aluminum alloy as the matrix metal may comprise heating the metal matrix composite to an elevated temperature, for example, to about 430° C., which is maintained for an extended period (e.g., 18–20 hours). The metal matrix may then be quenched in boiling water at about 100° C. for about 20 seconds (i.e., a T-4 heat treatment) which can temper or improve the ability of the composite to withstand tensile stresses.

Moreover, it is possible to use a reservoir of matrix metal to assure complete infiltration of the filler material and/or to supply a second metal which has a different composition from the first source of matrix metal. Specifically, in some cases it may be desirable to utilize a matrix metal in the reservoir which differs in composition from the first source of matrix metal. For example, if an aluminum alloy is used as the first source of matrix metal, then virtually any other metal or metal alloy which was molten at the processing temperature could be used as the reservoir metal. Molten metals frequently are very miscible with each other which would result in the reservoir metal mixing with the first source of matrix metal so long as an adequate amount of time is given for the mixing to occur. Thus, by using a reservoir metal which is different in composition from the first source of matrix metal, it is possible to tailor the properties of the metal matrix to meet various operating requirements and thus tailor the properties of the metal matrix composite.

A barrier means may also be utilized in combination with the present invention. Specifically, the barrier

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means for use with this invention may be any suitable means which interferes, inhibits, prevents or terminates the migration, movement, or the like, of molten matrix alloy (e.g., an aluminum alloy) beyond the defined surface boundary of the filler material. Suitable barrier 5 means may be any material, compound, element, composition, or the like, which, under the process conditions of this invention, maintains some integrity, is not volatile and preferably is permeable to the gas used with the process, as well as being capable of locally inhibit- 10 ing, stopping, interfering with, preventing, or the like, continued infiltration or any other kind of movement beyond the defined surface boundary of the ceramic filler. Barrier means may be used during spontaneous infiltration or in any molds or other fixtures utilized in connection with thermo-forming of the spontaneously infiltrated metal matrix composite, as discussed in greater detail below. Suitable barrier means includes materials which are substantially non-wettable by the migrating molten matrix alloy under the process conditions employed. A barrier of this type appears to exhibit little or no affinity for the molten matrix alloy, and movement beyond the defined surface boundary of the filler material or preform is prevented or inhibited by the barrier means. The barrier reduces any final machining or grinding that may be required of the metal matrix composite product. As stated above, the barrier preferably should be permeable or porous, or rendered permeable by puncturing, to permit the gas to contact the molten matrix alloy. Suitable barriers particularly useful for aluminum matrix alloys are those containing carbon, especially the crystalline allotropic form of carbon known as graphite. Graphite is essentially non-wettable by the molten alu- 35 minum alloy under the described process conditions. A particular preferred graphite is a graphite foil product that is sold under the trademark GRAFOIL (R), registered to Union Carbide. This graphite foil exhibits sealing characteristics that prevent the migration of molten $_{40}$ aluminum alloy beyond the defined surface boundary of the filler material. This graphite foil is also resistant to heat and is chemically inert. GRAFOIL (R) graphite foil is flexible, compatible, conformable and resilient. It can be made into a variety of shapes to fit any barrier appli-45 cation. However, graphite barrier means may be employed as a slurry or paste or even as a paint film around and on the boundary of the filler material or preform. GRAFOIL (R) is particularly preferred because it is in the form of a flexible graphite sheet. In use, this paper- 50 like graphite is simply formed around the filler material or preform. Other preferred barrier(s) for aluminum metal matrix alloys in nitrogen are the transition metal borides (e.g., titanium diboride (TiB₂)) which are generally non-wet- 55 table by the molten aluminum metal alloy under certain of the process conditions employed using this material. With a barrier of this type, the process temperature should not exceed about 875° C., for otherwise the barrier material becomes less efficacious and, in fact, 60 with increased temperature infiltration into the barrier will occur. Moreover, the particle size of the barrier material may affect the ability of the material to inhibit spontaneous infiltration. The transition metal borides are typically in a particulate form (1-30 microns). The 65 barrier materials may be applied as a slurry or paste to the boundaries of the permeable mass of ceramic filler material which preferably is preshaped as a preform.

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Other useful barriers for aluminum metal matrix alloys in nitrogen include low-volatile organic compounds applied as a film or layer onto the external surface of the filler material or preform. Upon firing in nitrogen, especially at the process conditions of this invention, the organic compound decomposes leaving a carbon soot film. The organic compound may be applied by conventional means such as painting, spraying, dipping, etc.

Moreover, finely ground particulate materials can function as a barrier so long as infiltration of the particulate material would occur at a rate which is slower than the rate of infiltration of the filler material.

Thus, the barrier means may be applied by any suitable means, such as by covering the defined surface boundary with a layer of the barrier means. Such a layer of barrier means may be applied by painting, dipping, silk screening, evaporating, or otherwise applying the barrier means in liquid, slurry, or paste form, or by sputtering a vaporizable barrier means, or by simply depositing a layer of a solid particulate barrier means, or by applying a solid thin sheet or film of barrier means onto the defined surface boundary. With the barrier means in place, spontaneous infiltration substantially terminates when the infiltrating matrix metal reaches the defined surface boundary and contacts the barrier means. Various demonstrations of the present invention are included in the Examples immediately following. However, these Examples should be considered as being illustrative and should not be construed as limiting the scope of the invention as defined in the appended claims.

EXAMPLE 1

This Example illustrates a technique for making a hollow metal matrix composite body by use of a mandrel comprising a non-infiltratable material. Specifically, this Example demonstrates that a metal matrix composite body, in the form of a hollow shell, can be fabricated by slip casting a filler material admixture to make a preform and then filling the interior of the resulting slip cast preform with an uninfiltratable particulate mass. FIGS. 1a and 1b show in schematic cross-sectional form the setup used to make a metal matrix composite body. A sphere measuring about 3 inches (76 mm) in diameter and having 12 regularly spaced truncations each measuring about 11/16 inch (17 mm) in diameter was spray coated with a Grade MS-122 fluorocarbon release agent dry lubricant (Miller Stevenson Company, Inc., Danbury, Conn.). A Grade GI-1000 rubber molding compound (Plastic Tooling Supply Company, Exton, Pa.) was cast around the spray coated sphere to form a rubber mold inversely replicating the shape of the sphere. After curing the rubber molding compound in air for about 12 hours, the spray coated sphere was separated from the mold. A wax model of the original sphere was then made by casting Grade 5550-K. GRN. FLK. molten wax (Yates Manufacturing Company, Chicago, Ill.) at a temperature of about 110° C. into the rubber mold cavity which remained after removing the sphere. The wax was then allowed to cool to substantially room temperature. After the wax had cooled to substantially room temperature, the wax model was separated from the rubber mold. A similar process was used to fabricate a wax model for the matrix metal reservoir portion of the subsequent investment casting. The

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reservoir measured about 4 inches (102 mm) in diameter and about 3 inches (76 mm) tall. Before solidification of the molten wax reservoir model, however, a steel mandrel was inserted into the wax; the subsequent solidification of the wax locked the mandrel in place.

The two wax models, that for the sphere itself and that for the matrix metal reservoir, were joined at one of the flat, circular truncations on the sphere to produce an investment pattern. The means of joining the two wax models comprised welding them together with addi- 10 tional molten wax.

In reference to FIG. 1a, an investment shell 102 com- prising CaCO₃ was then built up on the surface of the wax investment pattern. Specifically, the wax invest-

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600° C. The investment shell mold 102 was left in the approximately 600° C. furnace until it was ready to be used for the spontaneous infiltration process. The resultant mold comprised a spherical end portion that interconnected via a tubular neck region to an opened end cylinder.

About 1,126 grams of a slip comprising by weight about 53.3 percent 500 grit 39 CRYSTOLON (R) green silicon carbide (Norton Company, Worcester, Mass.), about 13.3 percent 1000 grit 39 CRYSTOLON (R) green silicon carbide, about 31.1 percent acetone, about 2.0 percent magnesium particulate (-325 mesh, Reade Manufacturing Company, Lakehurst, N.J.) and about 0.3 percent Q-PACTM polypropylene carbonate binder (Air Products and Chemicals, Inc., Emmaus, Pa.) was prepared. Specifically, the green silicon carbide and magnesium particulates were placed into a dry 8.9 liter porcelain ball mill (U.S. Stoneware Corp., Mahwah, N.J.) containing about 4000 grams of 15/16 inch (24 mm) diameter milling media (Standard Ceramic Supply) Co., a Division of Chem-Clay Corp., Pittsburgh, Pa.). After ball milling the particulates for about an hour, all but about 772 grams of ball milled particulates were removed from the mill. The removed ball milled particulates were sealed tightly in a NALGENE (R) plastic jar (Nalge Company, Rochester, N.Y.) and stored for subsequent use. The acetone and the Q-PACTM binder were added to the porcelain ball mill to form the slip. The slip was ball milled for about 1 hour. The slip was poured into the spherical portion of the mold discussed above until it was substantially full. A rubber stopper was inserted into the neck region 104 between the spherical portion of the mold and the attached cylindrical portion of the mold. Having isolated the two portions of the mold in this manner, the mold was rotated to permit the slip to coat evenly the surfaces of the spherical portion of the mold. Periodic removal of the rubber stopper and inspection of the slip casting process revealed that after approximately 5 minutes, a $\frac{3}{8}$ inch (10 mm) to $\frac{1}{2}$ inch (13 mm) thick coating had been built-up on the inner wall of the spherical portion of the mold. The remaining slip was poured from the mold. The resultant slip cast coating comprised a preform 106 whose inner surface was approximately spherical and whose outer surface closely matched that of the truncated sphere portion of the original wax investment pattern in size and shape. Loose 500 grit E38 ALUNDUM (R) alumina powder 108 (Norton Company, Worcester, Mass.) was then poured into the interior of the slip cast preform within the mold to a level substantially flush with the bottom of the neck region 104. The E38 ALUNDUM (R) alumina powder 108 was used as a mandrel because it was not infiltratable by molten metal under the processing conditions due primarily to the fact that the alumina material did not contain magnesium powder. Additional slip 110 was then poured into the neck region 104 and allowed to slip cast against the E38 ALUNDUM (R) 108 until a cast thickness of about $\frac{3}{8}$ inch (10 mm), to about $\frac{1}{2}$ inch (13 mm) was achieved, thereby eliminating any discontinuity in the preform 106. A dry filler admixture 112, having the same composition as the admixture which was utilized to make the slip, was then poured into the bottom of the upper half of the investment shell 102 until a depth of about $\frac{1}{4}$ inch (6 mm) was achieved. Magnesium particulate 114 (-50 mesh, Reade Manufacturing Company) was then sprinkled substantially uniformly over the top of the dry

ment pattern was dipped into a slip or slurry comprising 15 by weight about 30.0 percent NYACOL® 1430AT colloidal silica (Nyacol Products, Inc., an affiliate of PQ Corporation, Ashland, Mass.), about 66.1 percent HUBERCARB (R) Q 325 calcium carbonate (-325 mesh, J. M. Huber Corporation, Calcium Carbonate Div., 20 Quincy, Ill.), about 3.0 percent 500 grit TET-RABOR (R) boron carbide (Exolon-ESK Corporation, Tonawanda, N.Y.), about 0.6 percent VICTOWET (R) 12 wetting agent (Ransom and Randolph, Inc., Maumee, Ohio) and about 0.3 percent DCH Antifoam de- 25 foamer (Ransom and Randolph, Inc.). The slip coated wax model was then dusted or stuccoed with dry 90 grit RANCO (R) SIL No. A silica sand (Ransom and Randolph, Inc.). The wax model and its developing investment shell 102 were then dried for about $\frac{1}{2}$ hour at a 30 temperature of about 65° C. The dried investment shell 102 was then dipped for about 2 seconds into a bath of NYACOL (R) 1430 AT colloidal silica. This dip-dustdry-wet sequence was then immediately repeated. Next, the coated wax investment pattern was immediately 35 dipped into a secondary investment slurry comprising by weight about 1 part REDIP (R) indicator (Ransom and Randolph, Inc.), about 2 parts VICTOWET (R) 12 wetting agent, about 56 parts distilled water, about 274 parts NYACOL (R) 830 colloidal silica and about 700 40 parts RANCO (R) SIL No. 2 silica powder (Ransom and Randolph, Inc.) to yield a slurry viscosity corresponding to about 15 seconds in a Zahn Number 4 cup. The slurry coated investment shell was then stuccoed or dipped in a fluidized bed of approximately 30 grit RAN- 45 CO (R) SIL B silica sand (Ransom and Randolph, Inc.). The stuccoed investment shell was again dried at a temperature of about 65° C. for about $\frac{1}{2}$ hour or until the **REDIP** (R) indicator in the shell changed in color from yellow-green to deep orange. This second dip-stucco- 50 dry sequence was then repeated an additional four to five times. No prewetting of the investment shell with colloidal silica between dippings in the secondary investment shell slurry was required. The coated wax investment pattern was then placed into a steam auto- 55 clave to remove the wax pattern from the surrounding investment shell. After autoclaving at a temperature corresponding to a water vapor pressure of about 100 psi (690 kPa) for about five minutes, substantially all of the wax had been removed from the surrounding invest- 60 ment shell 102. The investment shell 102 was then removed from the steam autoclave and placed into a resistance heated air atmosphere furnace at substantially room temperature. The furnace temperature was then increased to about 850° C. at a rate of about 800° C. per 65 hour. After maintaining a temperature of about 850° C. for about $4\frac{1}{2}$ hours to rigidize the investment shell 102, the shell was furnace cooled to a temperature of about

filler material admixture 112 until a concentration of about 6 milligrams per square centimeter was obtained.

Several ingots of a matrix metal 116 comprising by weight about 12 percent silicon and the balance commercially pure aluminum, weighing a total of about 5 1200 grams, were placed on top of copper foil slings 118. The ends of the copper foil sling 118 were folded over the top edge of the investment shell 102 such that the ingots remained suspended over the magnesium particulate layer 114 and the filler material admixture 10 112 in the bottom of the upper half of the investment shell 102. A PERMA FOIL graphite foil cover sheet 120 (TTAmerica, Portland, Oreg.) sufficiently sized to cover the open end of the cylindrical portion of the investment shell 102, was placed over the matrix metal 15 108 inside of the metal matrix composite shell was **116**. As shown in FIG. 1b, the investment shell mold 102 and its contents were placed onto a stainless steel holder 122 and secured with copper foil straps 124. The stainless steel holder 122 and its contents were then placed 20 into a stainless steel can 126 measuring about 10 inches (254 mm) long by about 10 inches (254 mm) wide by about 10 inches (254 mm) tall. The bottom of the can 126 was covered with a graphite foil sheet 128 having substantially the same dimensions as the length and 25 width of the can 126. About 10 grams each of Grade RMC-3 magnesium turnings 130 (Reade Manufacturing) Company) and TI-LOY 97 titanium sponge 134 (Chemalloy Company, Bryn Mawr, Pa.) were placed into the can 126 outside of the stainless steel holder 122. The 30 titanium sponge 134 and magnesium turnings 130 together functioned as a "getter" to absorb oxygen from any oxygen-containing species in the car 126. Two copper foil sheets 132, each measuring about 16 inches (406 mm) long by about 14 inches (356 mm) wide by about 6 35 mils (0.15 mm) thick, were placed over the opening of the stainless steel can 126. The portions of the copper sheets 132 extending over the sides of the can 126 were folded down against the sides of the can **126** to form an isolated chamber. A nitrogen gas purge tube 136 was 40 provided through one side of the can 126. The stainless steel can 126 and its contents were placed into an electric resistance atmosphere furnace. A nitrogen gas flow rate of about 15 liters per minute through the purge tube 136 into the stainless steel can 45 **126** was established. The furnace was heated from about room temperature to a temperature of about 200° C. at a rate of about 400° C. per hour. After maintaining a temperature of about 200° C. for about 1 hour, the temperature was increased to about 520° C. at a rate of 50 about 400° C. per hour. After maintaining a temperature of about 520° C. for about 1 hour, the temperature was increased to about 780° C. at a rate of about 400° C. per hour. After maintaining a temperature of about 780° C. for about 3 hours, the nitrogen gas purge tube 136 was 55 disconnected. The stainless steel can 126 and its contents were removed from the furnace.

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116. After the stainless steel holder 122 and its contents had cooled substantially to room temperature, the investment shell mold 102 and its contents were removed from the holder 122. The investment shell mold 102 was removed with light hammer blows to reveal that at least some of the matrix metal **116** had infiltrated the slip cast preform 106 adjacent to the investment shell 102 to form a metal matrix composite body having substantially the same shape as the original near-spherical wax investment pattern. Residual matrix metal 116 was removed from the metal matrix composite body with a diamond saw. An approximately § inch (10 mm) diameter hole was then drilled in what was originally the neck region 104, 110 and the uninfiltrated alumina powder blown out with compressed air. Finally, the metal matrix composite body was sliced in half using a diamond saw to reveal a rough surface on the inside of the metal matrix composite shell. The 500 grit E38 ALUN-DUM (R) alumina powder 108 contained within the cavity of the slip cast preform was infiltrated an amount of less than 1/32 of an inch (0.8 mm).

EXAMPLE 2

This Example demonstrates that internal bolt threads can be fabricated in a metal matrix composite body by incorporating a removeable steel mandrel in the form of a bolt into an infiltratable mass of filler material.

A GRAFOIL (R) graphite foil (Union Carbide Company, Danbury, Conn.) box 10 measuring about $2\frac{1}{2}$ inches (64 mm) square and about 3 inches (76 mm) tall was fabricated from a single sheet of GRAFOIL (R) measuring about 0.015 inch (0.38 mm) thick by making strategically placed cuts and folds in the GRAFOIL (R) sheet and cementing the folds together with RIGID-LOCK (R) graphite cement (Polycarbon Corporation, Valencia, Calif.). The cemented folds were reinforced with strategically placed staples. About 300 grams of 500 grit 38 ALUNDUM (R) fused alumina powder was placed into a stainless steel tray measuring about 5 inches (127 mm) square and about 3 inches (76 mm) tall. The tray and its contents were placed into a vacuum drying oven and vacuum dried for about 12 hours at a temperature of about 150° C. under about 30 inches (762 mm) of mercury vacuum. The tray and its contents were then removed from the vacuum drying oven and the alumina powder was placed into a dry 1.1 liter porcelain ball mill (U.S. Stoneware Corporation, Mahwah, N.J.). About 60 grams of magnesium particulate (-325 mesh, Atlantic Equipment Engineers, Inc., Bergenfield, N.J.) was added to the ball mill. The ball mill lid was secured and the filler material admixture in the ball mill was roll mixed for about 15 hours. The roll-mixed filler material was then placed into the aforementioned stainless steel tray inside the approximately 150° C. vacuum drying oven. The filler material admixture 20 was vacuum dried at a temperature of

The copper foil sheets 132 and the stainless steel about 150° C. under about 30 inches (762 mm) of merholder 122 and its contents were removed from the cury vacuum for about 1 hour. The tray and its contents stainless steel can 126. The stainless steel holder 122 and 60 were removed from the vacuum drier. its contents were placed onto a water cooled copper In reference to FIG. 3, a stainless steel bolt 12 with a quench plate to permit directional solidification to octhreaded region measuring about $1\frac{1}{5}$ inches (29 mm) long by about $\frac{3}{6}$ inch (10 mm) in diameter was painted cur. To assist in the directional solidification of the with a uniform coating of DAG 154 colloidal graphite matrix metal, air was blown around the bottom of the 14 (Acheson Colloids Company, Port Huron, Mich.) stainless steel holder 122 adjacent to the water cooled 65 and dried in air at substantially room temperature for copper quench plate. In addition, FEEDOL (R) 9 hot about $\frac{1}{2}$ hour. Two additional colloidal graphite coattopping particulate mixture (Foseco, Inc., Cleveland ings were applied in a substantially similar fashion. The Ohio) was poured on top of the molten matrix metal

graphite coated stainless steel bolt 12, 14 was then placed substantially vertical in the center of the graphite foil box 10 and oriented such that the bolt head contacted the bottom of the box 10. An E38 ALUN-DUM (R) fused alumina 16 having a 500 grit (mean parti-5 cle size of about 17 microns) was poured into the graphite foil box 10 around the coated stainless steel bolt 12, 14 to a depth of about $\frac{1}{4}$ inch (6 mm) and leveled. A GRAFOIL (R) sheet 18 measuring about $2\frac{1}{2}$ inches (64) mm) square and having an approximately $\frac{3}{5}$ inch (10 10 mm) diameter hole in its center was placed into the graphite foil box 10 over the coated stainless steel bolt 12, 14 and contacting the layer of 38 ALUNDUM (R) fused alumina particulate material 16. The vacuum dried filler material admixture 20 was then poured into 15 the graphite foil box 10 around the coated stainless steel bolt 12, 14 to a level substantially flush with the top of the bolt. After leveling the filler material admixture 20, a matrix metal 22 measuring about 2 inches (51 mm) square and about 1 inch (25 mm) thick and weighing 20 about 177 grams and comprising commercially pure aluminum (Aluminum Association alloy number 170.1) was centered in the graphite foil box 10 to form a layup. The graphite foil box 10 was placed into a stainless 25 steel run can 24 measuring about 4 inches (102 mm) in diameter and about 4 inches (102 mm) tall. About 5 grams of TI-LOY 97 titanium sponge 26 (Chemalloy) Corporation, Bryn Mawr, Pa.) were placed into the stainless steel run can 24 around the graphite foil boat 30 10. A copper sheet 28 measuring about 6 inches (152 mm) square and about 6 mils (0.15 mm) thick was placed over the open-end of the stainless steel run can 24. Those portions of the copper sheet 28 extending over the sides of the can were folded down tightly 35 against the sides of the run can 24 to form an isolated chamber. A nitrogen gas purge tube 30 was provided through one side of the can 24. The stainless steel can 24 and its contents were placed into a resistance heated air atmosphere furnace. A nitro-40 gen gas flow rate of about 5 liters per minute was established. The furnace chamber was then heated from substantially room temperature to a temperature of about 600° C. at a rate of about 500° C. per hour. At a temperature of about 600° C., the nitrogen gas flow rate 45 was reduced to about 1 liter per minute. The temperature was then increased to about 800° C. at a rate of about 500° C. per hour. After maintaining a temperature of about 800° C. for about 1 hour, the nitrogen gas purge tube 30 was disconnected and the stainless steel 50 run can 24 and its contents were removed from the furnace and set on a refractory plate to cool. After cooling to substantially room temperature, the copper sheet 28 over the top of the stainless steel run can 24 was removed and the graphite foil boat 10 and its contents 55 were removed from the run can 24. Peeling away the graphite foil 10 from the sides of the lay-up revealed that the matrix metal 23 had infiltrated the filler material admixture 20 around the threaded portion of the coated stainless steel bolt 12, 14 to produce a metal matrix 60 composite body. The 38 ALUNDUM (R) fused alumina particulate material 16 below the graphite foil divider sheet 18 was not infiltrated as it did not contain any infiltration enhancer precursor. The colloidal graphite coating 14 on the stainless steel bolt 12 prevented a 65 reaction and therefore a bond from developing between the matrix metal in the composite and the steel in the bolt. Thus, the coated stainless steel bolt could be re-

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moved from the formed composite simply by unscrewing the bolt back out of the composite body. The resulting threaded bore in the metal matrix composite body shows that it is possible to form a metal matrix composite body containing a threaded passageway through the use of a removable threaded mandrel incorporated into a filler material.

EXAMPLE 3

This Example demonstrates that a metal matrix composite body containing at least one smooth circular hole can be fabricated by incorporating removable round mandrels into a filler material admixture or preform. In reference to FIG. 3, graphite fixture 40 having an

interior measuring about $6\frac{1}{8}$ inches (156 mm) square and having a height of about 6 inches (152 mm) and open on both ends was placed and substantially centered in a graphite boat 42 with interior dimensions measuring about 9 inches (229 mm) square and about 4 inches (102 mm) in height.

A GRAFOIL (R) graphite foil (Union Carbide Company, Danbury, Conn.) box 44 having substantially the same dimensions as the interior of the graphite fixture 40 was fabricated from a single sheet of GRAFOIL (R) measuring about 0.015 inch (0.38 mm) thick by making a strategically placed cuts and folds in the GRA-FOIL (R) sheet and cementing the folds together with RIGIDLOCK (R) graphite cement (Polycarbon Corporation, Valencia, Calif.). The cemented folds were reinforced with strategically placed staples.

A graphite plate 46 measuring about 6 inches (152 mm) square and about $\frac{1}{2}$ inch (13 mm) thick and containing four $\frac{1}{2}$ inch (13 mm) diameter holes with centers located approximately 1 inch (25 mm) from each corner of the graphite plate 46 was placed into the graphite foil box 44 on the base of the graphite boat 42. Four stainless steel tubes 48, measuring about $\frac{1}{2}$ inch (25 mm) in diameter and about 2 inches (51 mm) long, were coated with RIGIDLOCK (R) colloidal graphite cement (0.13 mm) and wrapped with one layer of GRAFOIL (R) 50 measuring about 0.005 inch (0.13 mm) thick. The GRA-FOIL (R) coated stainless steel tubes 48, 50 were then inserted into the holes in the graphite plate 46. About 700 grams of 54 grit 39 CRYSTOLON® green silicon carbide (Norton Company, Worcester, Mass.) and about 300 grams of 90 grit 39 CRYS-TOLON (R) green silicon carbide were placed into a dry 8.9 liter porcelain ball mill (U.S. Stoneware Corporation, Mahwah, N.J.) containing about 2000 grams of alumina milling media (Standard Ceramic Supply Company, a Division of Chem-Clay Corporation, Pittsburgh, Pa.) each measuring about 15/16 inch (24 mm) in diameter. The lid to the ball mill was secured and the 39 CRYSTOLON (R) silicon carbide was ball milled dry for about 24 hours. After ball milling, the milling media was removed and about 20 grams of magnesium particulate (-325 mesh, Hart Corporation, Tamaqua, Pa.) was added to the mill. The lid was resecured and the filler material admixture 52 was roll mixed for about 2 hours. About 967 grams of the roll mixed filler material admixture 52 were poured into the graphite foil box 44 around the GRAFOIL (R) coated stainless steel tubes 48, 50 on top of the graphite plate 46 and leveled. About 5 grams of magnesium particulate 54 (-100 mesh, Hart Corporation) was sprinkled substantially uniformly over the top surface of the filler material admixture 52. A GRA-FOIL (R) graphite foil feeder box 56 measuring about $5\frac{7}{8}$ inches (149 mm) square, about 2 inches (51 mm) tall,

open on one end, and on its base having four approximately $\frac{1}{2}$ inch (17 mm) diameter holes located so as to substantially coincide with the GRAFOIL (R) coated stainless steel tubes 48, 50 and an approximate $2\frac{1}{2}$ inch (64 mm) diameter feed hole was placed into the center 5 of the base of the graphite foil box 56 and contacted with the magnesium particulate layer 54 on top of the filler material admixture 52. A gating means comprising a graphite riser ring 58 measuring about $2\frac{1}{2}$ inches (64) mm) in inside diameter and about $\frac{1}{2}$ inch (13 mm) tall, 10 was cemented to the graphite foil feeder box 56 with RIGIDLOCK (R) graphite cement. The inside of the graphite riser ring 58 was filled about half-way with the aforementioned filler material admixture 52 and the remaining half with magnesium particulate 54 (-100 15 mesh, Hart Corporation). A particulate barrier material 60 comprising an admixture of by weight about 15 percent Grade F-69 glass frit (Fusion Ceramics Inc., Carrollton, Ohio) and the balance substantially equal weight fractions of 90 grit, 220 grit and 500 grit E1 20 ALUNDUM (R) fused alumina (Norton Company) was poured into the graphite foil feeder box 56 to a level substantially flush with the top of the graphite riser ring 58 but somewhat higher out near the walls of the box. A matrix metal 62 ingot weighing about 1457 grams mea- 25 suring about 3 inches (76 mm) square and about $3\frac{5}{8}$ inches (92 mm) tall and comprising by weight about 12 percent silicon and the balance aluminum, was placed into the GRAFOIL (R) feeder box 56 and centered over the graphite riser ring 58 to form a lay-up. 30 The graphite boat 42 and its contents were placed into an electric resistance controlled atmosphere furnace (retort) at substantially room temperature. The retort was sealed, evacuated to about 30 inches (762) mm) of mercury vacuum and backfilled with nitrogen 35 gas to establish a flow rate of about 4 liters per minute at substantially atmospheric pressure. The temperature in the retort was then increased to about 200° C. at a rate of about 200° C. per hour. After maintaining a temperature of about 200° C. for about 5 hours, the 40 temperature was then increased to about 800° C. at a rate of about 200° C. per hour. After maintaining a temperature of about 800° C. for about 6 hours, the temperature was decreased to about 700° C. at a rate of about 200° C. per hour. At a temperature of about 700° 45 C., the graphite boat 42 and its contents were removed from the retort and placed onto a water cooled aluminum quench plate. Additionally, FEEDOL (R) No. 9 hot topping particulate mixture 60 was poured over the residual molten matrix metal 62. To assist in the direc- 50 tional solidification of the matrix metal, a CERA-BLANKET (R) ceramic fiber blanket (Manville Refractory Products, Denver, Colo.) measuring about 2 inches (51 mm) thick was placed over the top and sides of the graphite boat 42. After cooling to substantially room 55 temperature, the lay-up was removed from the graphite boat 42 and the bedding particulate admixture 60 of glass frit and alumina was removed with light hammer blows to reveal that the matrix metal 62 had infiltrated the filler material admixture 52 around the GRA-60 FOIL (R) wrapped tubes 48, 50 to produce a metal matrix composite body. The GRAFOIL (R) wrapping 50 on the stainless steel tubes 48 prevented any reaction and therefore any bonding from occurring between the matrix metal 62 and the steel tubes 48. The stainless steel 65 tubes 48 were easily pushed out from the metal matrix composite body formed around them, leaving four, smooth, circular through-holes in the formed metal

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matrix composite body. Thus, this Example illustrates that a metal matrix composite body containing through holes of a simple geometry can be fabricated by incorporating a removable mandrel into the preform or filler material admixture.

What is claimed is:

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1. A method of making a metal matrix composite containing at least one cavity or channel therein, comprising:

forming at least one permeable mass of at least one filler or at least one preform of at least one filler, said at least one permeable mass defining at least one cavity or channel therein;

providing at least one bed or mass of particles in at

least a portion of said at least one cavity or channel; providing at least one matrix metal;

spontaneously infiltrating at least a portion of the at least one permeable mass with at least one molten matrix metal up to said at least one bed or mass of particles, wherein said at least one bed or mass of particles comprises a means not capable of being spontaneously infiltrated by said at least one molten matrix metal; and

removing said at least one bed or mass of particles from the spontaneously infiltrated at least one permeable mass to form said at least one cavity or channel in said infiltrated mass, wherein said at least one cavity or channel corresponds in shape to said at least one bed or mass of particles, thereby forming said metal matrix composite.

2. The method of claim 1, further comprising providing at least one additional shape defining means in at least a portion of said at least one cavity or channel of said at least one permeable mass.

3. The method of claim 2, wherein said at least one additional shape defining means comprises at least one material selected from the group consisting of (1) at least one mandrel which is capable of surviving the spontaneous infiltration conditions and (2) at least one coating on at least one additional substrate material, wherein said at least one coating results in said at least one substrate material being capable of surviving the spontaneous infiltration conditions. 4. The method of claim 3, wherein said at least one coating comprises at least one barrier. 5. The method of claim 2, wherein said at least one additional shape defining means comprises at least one mandrel coated with at least one barrier means. 6. The method of claim 1, wherein said removing of said at least one bed or mass of particles comprises at least one procedure selected from the group consisting of oxidizing at least a portion of said at least one bed or mass of particles, leaching at least a portion of said at least one bed or mass of particles and physically or mechanically removing at least a portion of said at least one bed or mass of particles.

7. The method of claim 1, wherein said at least one bed or mass of particles comprises alumina, wherein said alumina is not capable of being spontaneously infiltrated by said at least one matrix metal under the process conditions. 8. The method of claim 1, wherein said at least one bed or mass of particles is removable from said metal matrix composite body by at least one process selected from the group consisting of air blasting, grit blasting, leaching and physical agitation. 9. The method of claim 1, further comprising communicating at least one infiltrating atmosphere with at least

one of said at least one permeable mass and said at least one matrix metal for at least a portion of the period of infiltration.

10. The method of claim 1, further comprising positioning at least one infiltration enhancer within at least ⁵ a portion of said at least one permeable mass.

11. The method of claim 10, wherein at least one infiltrating atmosphere communicates with at least one of said at least one permeable mass and said at least one 10matrix metal for at least a portion of the period of infiltration and wherein said infiltration enhancer is formed from at least one reaction between at least one infiltration enhancer precursor and said at least one infiltrating atmosphere. 12. The method of claim 12, wherein said at least one infiltration enhancer precursor comprises magnesium, said at least one infiltrating atmosphere comprises nitrogen, said infiltration enhancer comprises at least one 20 nitride of magnesium and said at least one matrix metal comprises aluminum. 13. A method of making a metal matrix composite containing at least one cavity or channel therein, comprising: 25

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trated by said at least one matrix metal under the process conditions; and

removing said at least one bed or mass of particles from the spontaneously infiltrated at least one permeable mass to form said at least one cavity or channel in said infiltrated mass, wherein said at least one cavity or channel corresponds in shape to said at least one bed or mass of particles, thereby forming said metal matrix composite.

14. The method of claim 13, further comprising providing at least one additional shape defining means in at least a portion of said at least one cavity or channel of said at least one permeable mass.

15. The method of claim 14, wherein said at least one

- forming at least one permeable mass of at least one filler or at least one preform of at least one filler, said at least one permeable mass defining at least one cavity or channel therein and being substantially nonreactive with matrix metal under the pro- 30 cessing conditions;
- providing at least one bed or mass of particles in at least a portion of said at least one cavity or channel of said at least one permeable mass;

providing at least one matrix metal;

providing at least one material comprising at least one of at least one infiltration enhancer precursor and at least one infiltration enhancer to at least one of said at least one permeable mass and said at least one matrix metal;

15 additional shape defining means comprises at least one mandrel coated with at least one barrier means.

16. The method of claim 13, wherein said removing of said at least one bed or mass of particles comprises at least one procedure selected from the group consisting of oxidizing at least a portion of said at least one bed or mass of particles, leaching at least a portion of said at least one bed or mass of particles and physically or mechanically removing at least a portion of said at least one bed or mass of particles.

5 17. The method of claim 13, wherein said at least one matrix metal comprises aluminum.

18. The method of claim 17, wherein said at least one infiltration enhancer precursor comprises magnesium.

19. The method of claim 17, wherein said at least one bed or mass of particles comprises alumina, wherein said alumina is not capable of being spontaneously infiltrated by said at least one matrix metal under the process conditions.

20. The method of claim 13, wherein said at least one 35 bed or mass of particles comprises alumina, wherein said alumina is not capable of being spontaneously infiltrated by said at least one matrix metal under the process conditions.

providing at least one infiltrating atmosphere; causing said at least one matrix metal to become molten;

spontaneously infiltrating said at least one permeable 45 mass with said at least one molten matrix metal up to said at least one bed or mass of particles, wherein said at least one bed or mass of particles comprise a means not capable of being spontaneously infil-

21. The method of claim 13, wherein said at least one 40 infiltration enhancer precursor is provided in at least a portion of at least one of said at least one matrix metal, said at least one infiltrating atmosphere and said at least one permeable mass.

22. The method of claim 21, wherein said at least one infiltration enhancer precursor comprises magnesium, said at least one matrix metal comprises aluminum and said at least one infiltrating atmosphere comprises nitrogen.

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